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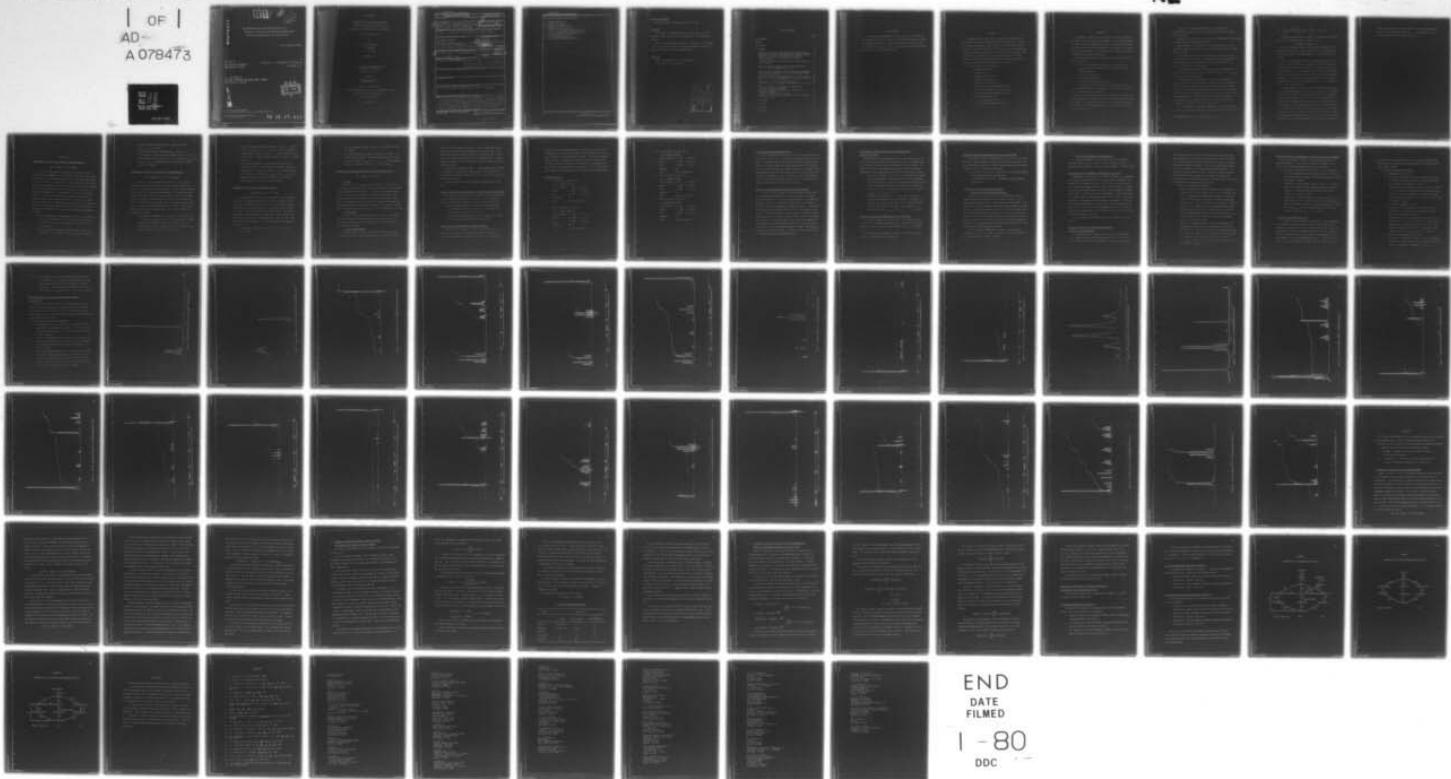
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THE PREPARATION OF SOME NOVEL ELECTROLYTES:
SYNTHESIS OF PARTIALLY FLUORINATED ALKANESULFONIC
ACIDS AS POTENTIAL FUEL CELL ELECTROLYTES

FINAL TECHNICAL REPORT

PREPARED BY

THE AMERICAN UNIVERSITY
WASHINGTON, DC 20016

BY

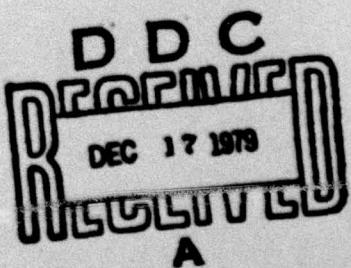
C. BUNYAGIDJ, H. PIETROWSKA, M. H. ALDRIDGE

SEPTEMBER 1979

TO

U.S. ARMY MOBILITY
EQUIPMENT RESEARCH AND DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA

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THE PREPARATION OF SOME NOVEL ELECTROLYTES:
SYNTHESIS OF PARTIALLY FLUORINATED ALKANE
SULFONIC ACIDS AS POTENTIAL FUEL CELL ELECTROLYTES

Final Technical Report

by

Chaiyun Bunyagidj

H. Pietrowska

M. H. Aldridge

September 1979

to

U. S. Army Mobility Equipment Research
and Development Command

Fort Belvoir, Virginia

Prepared by

The American University
Washington, D. C.

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The following acids have been prepared:

1. Methanedisulfonic acid
2. Ethanesulfonic acid
3. Ethane-1,2-disulfonic acid
4. Propane-1,3-disulfonic acid
5. Propane-1,2,3-trisulfonic acid
6. 2-Chloro-1,1,2-trifluoroethanesulfonic acid
7. 1,2,2-Trifluoroethane-1,1,2-trisulfonic acid
8. 1,1,2,3,3-Hexafluoropropanesulfonic acid
9. 2-Fluoroethanesulfonic acid
10. 2,2,2-Trifluoroethanesulfonic acid
11. 2,2,3,3-Tetrafluoropropanesulfonic acid

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TABLE OF CONTENTS

	Page
Acknowledgment	i
Abstract	ii
Introduction	1
Experimental	5
Preparation of Partially Fluorinated Alkyl Methanesulfonates	5
Preparation of Partially Fluorinated Alkyl p-Toluenesulfonates	6
Preparation of Partially Fluorinated Alkyl Bromides	7
Reaction of Partially Fluorinated Alkyl Halides With Sodium Sulfite	8
Conversion of Partially Fluorinated Sodium Alkanesulfonates Into Free Acids	9
Addition of Sodium Hydrogen Sulfite to Hexafluoropropene	9
1,1,2,3,3,3-Hexafluoropropanesulfonic Acid	12
Addition of Sodium Hydrogen Sulfite to Chlorotrifluoroethylene	12
Acidification of Crude Sodium Chlorotrifluoroethanesulfonate With 35% Sulfuric Acid	13
Hydrolysis of Chlorotrifluoroethanesulfonic Acid Ethyl Ester	13
Reaction of Chlorotrifluoroethanesulfonic Acid With Ethyl Ether	14
Preparation of 2,2,2-Trifluoroethyl Thiocyanate	14
Oxidation of 2,2,2-Trifluoroethyl Thiocyanate With Nitric Acid	15
Reaction of Partially Fluorinated Alkyl Bromides and Tosylates With Benzyl Mercaptan	15
Reaction of Partially Fluorinated Alkyl Tosylates With Tert-butyl Mercaptan	17
Oxidation of the Sulfides with Cl ₂ /H ₂ O	17
Hydrolysis of Partially Fluorinated Alkanesulfonyl Chlorides to Sulfonic Acids	19
nmr Spectra	20
Discussion	46
Conclusions	62
References	63

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ABSTRACT

The objective of this research was to prepare some strong acids for evaluation by Fort Belvoir as potential fuel cell electrolytes. The major acid, other than phosphoric, H_3PO_4 , currently under investigation by Fort Belvoir as a fuel cell electrolyte is TFMSA, $CF_3SO_3H \cdot H_2O$, trifluoromethane-sulfonic acid monohydrate aqueous solutions and sodium salt mixtures. TFMSA has been found to be superior to H_3PO_4 from the standpoint of electrode kinetics, but certain undesirable characteristics (volatility; wetting of Teflon) led to this search for a better fuel cell electrolyte.

The following acids have been prepared:

1. Methanesulfonic acid
2. Ethanesulfonic acid
3. Ethane-1,2-disulfonic acid
4. Propane-1,3-disulfonic acid
5. Propane-1,2,3-trisulfonic acid
6. 2-Chloro-1,1,2-trifluoroethanesulfonic acid
7. 1,2,2-Trifluoroethane-1,1,2-trisulfonic acid
8. 1,1,2,3,3,3-Hexafluoropropanesulfonic acid
9. 2-Fluoroethanesulfonic acid
10. 2,2,2-Trifluoroethanesulfonic acid
11. 2,2,3,3-Tetrafluoropropanesulfonic acid

INTRODUCTION

Improvements in H_3PO_4 fuel cell performance over the last decade have been due principally to engineering refinements. The ultimate performance will depend to a certain degree upon the fuel cell electrolyte and recent studies have indicated that TFMSA monohydrate, $CF_3SO_3H \cdot H_2O$, is far superior to H_3PO_4 from the standpoint of electrode kinetics. The present research is concerned with electrolyte improvement.

The properties desired for the ideal fuel cell electrolyte based on previous studies are:

1. It must be a moderately strong, highly water-soluble acid.
2. It must be thermally stable and non-volatile under fuel cell operating conditions.
3. It must be non-oxidizing.
4. It must be non-hydrolyzable.
5. Its solutions must be highly conductive.
6. It must be non-corrosive toward cell and electrode materials.

A literature search indicated several probable organic acid electrolytes, with their methods of preparation.

Berrick (1, 2) and Coffman (3) prepared $CHF_2CF_2SO_3H$ in a 54% yield from tetrafluoroethylene by the addition of sodium sulfite using benzoyl peroxide as a catalyst. The reaction was carried out in an autogeneous pressure at 30° to $210^\circ C$. The fluoroalkanesulfonic acid was generated from the sodium salt by sulfuric acid.

Kashar, et al. (4) prepared $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}$, $\text{C}_3\text{H}_7\text{CFHCF}_2\text{SO}_3\text{H}$ and $\text{C}_5\text{H}_{11}\text{CFHCF}_2\text{SO}_3\text{H}$ in good yields from the fluoroolefins and sodium hydrogen sulfite and borax.

Haszeldine (5) using sodium bisulfite and borax, prepared $\text{CFCl}_2\text{CF}_2\text{CFHCF}_2\text{SO}_3\text{H}$ and other chlorofluoroalkanesulfonic acids.

Another method for the preparation of fluoroalkanesulfonic acids was reported by Haszeldine and Kidd (6), who oxidized $(\text{CF}_3\text{S})_2\text{Hg}$ with 35% hydrogen peroxide at 105°C .

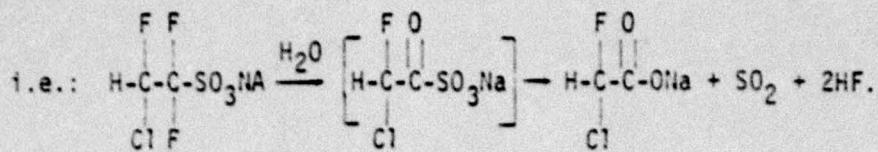
The end product of the oxidation of mercaptans, sulfides, disulfides, sulfones, etc., is a sulfonic acid. Oxidation by potassium permanganate (7), chromic anhydride (7), bromine water (8), hydrogen peroxide (9), nitric acid (10), and alkalis (11) are reported.

Many halogen compounds react with sodium, potassium or ammonium sulfites to give high yields of sulfonic acid salts (12, 13, 14), i.e., alkylation of alkali sulfites (Strecker).

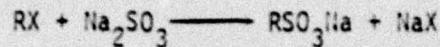
The first method that we selected for evaluation was Haszeldine's method, the addition of sodium hydrogen sulfite to alkenes in the presence of borax, because a variety of fluorinated alkenes were available commercially (PCR).* This procedure required the use of a Parr pressure reaction vessel and we soon encountered difficulties with leaks and corrosion. Other disadvantages to this procedure were the low yields due to the number of byproducts formed. For example, $4 \text{ CF}_2=\text{CFCl} + 4 \text{ NaHSO}_3 \rightarrow \text{HCF}_2\text{CFClSO}_3\text{Na} + \text{HCF}_2\text{COONa} + \text{HCFClCF}_2\text{SO}_3\text{Na} + \text{HCFClCOONa} + 2 \text{ SO}_2 + 4 \text{ HF}$.

The difluoroacetic acid derivative apparently results from the lability of the fluorine atoms which are removed from the α -carbon atom by hydrolysis.

*PCR Research Chemicals, Inc., Gainesville, Florida.



The second method evaluated was Strecker's method involving the reactions of alkyl halides with alkali sulfites, i.e.:



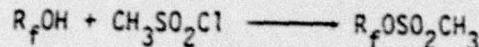
Using this procedure, methane disulfonic acid, ethanesulfonic acid, ethane 1,2-disulfonic acid, propane 1,3-disulfonic acid, propane 1,2,3-trisulfonic acid and 1,2,2-trifluoroethane 1,1,2-trisulfonic acid were prepared.

2,2,2-Trifluoroethanesulfonic acid was prepared by the nitric acid oxidation of 2,2,2-trifluoroethyl thiocyanate. The latter was obtained from 2,2,2-trifluoroethanol by converting it into mesylate according to Crossland and Servis (15) which was then reacted with sodium thiocyanate according to Crossland, Wells and Shiner (16) to yield the corresponding thiocyanate. We found that the nitric acid oxidation of the crude thiocyanate compound gave 2,2,2-trifluoroethanesulfonic acid of high purity, but the overall yield was only 20%.

2-Fluoroethanesulfonic acid, 2,2,2-trifluoroethanesulfonic acid and 2,2,3,3-tetrafluoropropanesulfonic acid were prepared by the introduction of sulfur into the partially fluorinated alkyl alcohols with subsequent oxidation to the respective sulfonic acids. This was accomplished by reacting the p-toluenesulfonates of the partially fluorinated alcohols (2-fluoroethanol, 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoropropanol) with the sodium salt of benzyl or t-butyl mercaptan to yield the corresponding benzyl or t-butyl partially fluorinated alkyl sulfides. These sulfides were then subjected to oxidative chlorination to give the corresponding partially fluorinated alkanesulfonyl chlorides which were subse-

quently hydrolyzed with water to the partially fluorinated alkanesulfonic acids. Of the two possible routes, that utilizing the benzyl mercaptan proved to be more efficient and gave higher yields.

EXPERIMENTAL

Preparation of Partially Fluorinated Alkyl Methanesulfonates

In a 2-liter three-necked flask equipped with a mechanical stirrer, dropping funnel, thermometer and reflux condenser fitted with a drying tube were placed 1 liter of methylene chloride, 1 mole of the appropriate alcohol, and 1.14 mole (115 g) of triethylamine. The latter was previously refluxed over phthalic anhydride, distilled, and redistilled, from potassium hydroxide pellets. The flask was placed in a cooling bath and 1.10 mole (126 g) of redistilled methanesulfonyl chloride was added at 0-10°C over a period of one hour. The stirring was continued for an additional 15 minutes. The reaction mixture was then washed twice with 300 ml aliquots of ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the residue vacuum distilled. The following compounds were prepared by this method:

1. 2,2,2-Trifluoroethyl methanesulfonate, yield 90%, b.p. 97-99°/35 mm, (lit. (15) 97-99°C 35 mm). The 1H nmr spectrum (CD_3COCD_3) showed a singlet at 3.24 ppm (3H) and a quartet at 4.75 ppm (2H, $J_{H,F} = 8.4$ Hz) Figure 1.
2. 1,1,1,3,3,3-Hexafluoro-2-propyl methanesulfonate, yield 87%, p.b. 156-157°C (lit. (15) 156-158°C). The 1H nmr spectrum (CD_3COCD_3)

showed a singlet at 3.35 ppm (3H) and a septet at 5.73 ppm (1H, $J_{H,F} = 5.7$ Hz) Figure 2.

3. 2,2,3,3-Tetrafluoropropyl methanesulfonate, yield 81%, b.p. 117-118°C/18 mm. The ^1H nmr spectrum showed a singlet at 3.15 ppm (3H), methine proton at 6.05 ppm (1H), split triplet ($J_{H,F\text{ gem}} = 53$ Hz, $J_{H,F\text{ vic}} = 5$ Hz), and methylene protons at 4.60 ppm (2H, triplet, $J_{H,F} = 13$ Hz) Figure 3.

Preparation of Partially Fluorinated Alkyl p-Toluenesulfonates

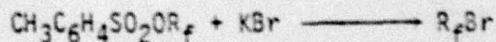


A mixture of 1 mole of the appropriate alcohol, 1.1 mole (175 g) of p-toluene sulfonyl chloride and 350 ml of water was heated to 50°C, and a solution of 1.1 mole (44 g) of sodium hydroxide in 170 ml of water was added with stirring at a rate such that the temperature of the reaction mixture was kept below 60°C. The stirring was continued until the solution became neutral. The reaction mixture was cooled and the tosylate extracted with ether. The ethereal extract was washed twice with concentrated ammonia and twice with water, and dried over anhydrous sodium sulfate. The solvent was removed, and the residue vacuum distilled. The following compounds were prepared by this method.

1. 2-Fluoroethyl p-toluenesulfonate, yield 55%, b.p. 143-146°C/1.2 mm (lit. (17) b.p. 138.5-140°C/1 mm). The ^1H nmr spectrum (CD_3COCD_3) showed aromatic protons at 7.61 ppm (4H, quartet, $J = 8$ Hz), ethylene protons at 5.01, 4.57 and 4.13 ppm (4H, multiplets), and methyl protons at 2.45 ppm (3H, singlet) Figure 4.

2. 2,2,2-Trifluoroethyl p-toluenesulfonate, yield 89%, b.p. 102-104°C/0.8 mm, m.p. 40-41°C (lit. (17) m.p. 41°C). The ^1H nmr spectrum showed aromatic protons at 6.6 ppm (4H, quartet), methylene protons at 3.5 ppm (2H, quartet) and methyl protons at 1.5 ppm (3H, singlet) Figure 5.
3. 2,2,3,3-Tetrafluoropropyl p-toluenesulfonate yield 64%, b.p. 149-155°C/4.0-4.7 mm. The ^1H nmr spectrum (CD_3COCD_3) showed aromatic protons at 7.65 ppm (4H, quartet, $J = 8$ Hz), methine proton at 6.25 ppm (1H, split triplet, $J_{\text{H},\text{F}\text{ gem}} = 52$ Hz, $J_{\text{H},\text{F}\text{ vic}} = 5$ Hz) methylene protons at 4.56 ppm (2H, triplet, $J_{\text{H},\text{F}} = 13$ Hz) and methyl protons at 2.42 ppm (3H, singlet) Figure 6.

Preparation of Partially Fluorinated Alkyl Bromides



In a three-necked flask fitted with a mechanical stirrer, thermometer, and a take-off adapter were placed 0.35 mole of the corresponding fluorinated alkyl p-toluenesulfonate, 0.71 mole (41.5 g) of anhydrous potassium bromide and 150 ml of diethyleneglycol. The reaction mixture was heated to 160-170°C. At 150°C, evolution of the bromide started. The reaction mixture was stirred continuously to prevent frothing and plugging of the take-off tube. The distillate was washed several times with water, dried over Drierite and fractionated. The following compounds were prepared by this method:

1. 2-Fluoroethyl bromide, yield 68% b.p. 70-71°C (lit. (18) b.p. 71.5-71.8°C).

2. 2,2,2-Trifluoroethyl bromide, yield 79%, b.p. 25.5-26°C (lit. (19) b.p. 26.3°C).
3. 2,2,3,3-Tetrafluoropropyl bromide, yield 95%, b.p. 68-69°C. The ^1H nmr spectrum (CD_3COCD_3) showed the methine proton at 6.16 ppm (1H, split triplet, $J_{\text{H},\text{F}}$ gem = 53 Hz, $J_{\text{H},\text{F}}$ vic = 4 Hz) and methylene protons at 3.78 ppm (2H, triplet, $J_{\text{H},\text{F}} = 15$ Hz) Figure 7.

Reaction of Partially Fluorinated Alkyl Halides with Sodium Sulfite



A. In Water

A solution of 20 g (0.16 mole) of sodium sulfite in 100 ml of water was placed in a three-necked flask fitted with mechanical stirrer, efficient reflux condenser and dropping funnel. 0.15 mole of the halide was added slowly with stirring over a period of two hours at about 50-60°C. The reaction mixture was refluxed gently with stirring for 48 hours. After cooling, the unreacted halide (if present) was separated, the aqueous layer evaporated to dryness, and the residue extracted with hot ethanol. Evaporation of ethanol gave the crude sodium salt of the corresponding sulfonic acid.

B. In 50% Ethanol

A mixture of 7 g (0.05 mole) of sodium sulfite, 80 ml of 50% ethanol and 0.05 mole of the halide was refluxed with stirring for 48 hours. It was cooled, filtered, the filtrate evaporated to dryness, and the solid residue worked up as above.

C. In Parr Pressure Reactor

A solution of 40 g (0.32 mole) of sodium sulfite dissolved in 200 ml of water and 0.30 mole of the halide were placed in a liter Parr pressure

reactor, and slowly heated with stirring. Usually at about 90°C an exothermic reaction started and the temperature rose to about 125°C. After the exothermic process subsided, the reactor was heated at 100°C for 12-16 hours. The reaction mixture was cooled, the unreacted halide (if present) separated, the aqueous solution evaporated to dryness, and the solid residue worked up as above.

The results are tabulated in Table I. The approximate yields are based on the amounts of crude sulfonate salts isolated. The ir spectra of all salt samples showed distinct absorption at 1160 and 1060 cm^{-1} characteristic for sulfonic acid salts.

The salts obtained from alkyl iodides were contaminated with sodium iodide.

Conversion of Partially Fluorinated Sodium Alkanesulfonates Into Free Acids

A 10% aqueous solution of the sodium alkane sulfonate was passed through an ion-exchange column packed with IR-120 resin. The collected aqueous solution of the acid was evaporated, and the residue vacuum distilled.

Using this procedure samples of the following acids were prepared:

1. 2-Fluoroethanesulfonic acid, yield 23%, b.p. 150-151°C/1.7 mm, neutralization equivalent 127 (calcd. 128).
2. 2,2,3,3-Tetrafluoropropanesulfonic acid, yield 58%, b.p. 90-91°C/0.4 mm, neutralization equivalent 191 (calcd. 196).

Addition of Sodium Hydrogen Sulfite to Hexafluoropropene

A mixture of 60 g (0.5 mole) of sodium hydrogen sulfite, 27.4 g of borax, 120 ml of water and 0.8 g of benzoyl peroxide were placed in a 1 liter Parr bomb reactor. The reactor was cooled in a dry ice-acetone

mixture and liquified perfluoropropene was introduced by suction into the evacuated bomb. The contents were heated to room temperature (25°C), the pressure measured, and the heating was continued. At $70\text{-}75^{\circ}\text{C}$ an exothermic reaction started. The heating was continued at 120°C for about 12 hours. The reactor contents were cooled to room temperature, the unreacted hexa-fluoropropene liquified and weighed, the reaction mixture filtered, evaporated to dryness, and the resulting salts extracted with hot absolute ethanol.

Experimental Results

I. 90 g (0.6 mole) of $\text{CF}_3\text{CF} = \text{CF}_2$

0.8 g of benzoyl peroxide

Initial Condition $T = 25^{\circ}\text{C}$ $P = 160$ psi

Maximum $T = 140^{\circ}\text{C}$ $P = 350$ psi

Final $T = 25^{\circ}\text{C}$ $P = 100$ psi

Conversion 37%

Yield 8.6 g of sodium salt

II. 98.8 g (0.66 mole) of $\text{CF}_3\text{CF} = \text{CF}_2$

0.8 g of benzoyl peroxide

Initial Condition $T = 25^{\circ}\text{C}$ $P = 180$ psi

Maximum $T = 150^{\circ}\text{C}$ $P = 400$ psi

Final $T = 25^{\circ}\text{C}$ $P = 120$ psi

Conversion 32%

Yield 11.5 g of sodium salt

III. 90.0 g (0.6 mole) of $\text{CF}_3\text{CF} = \text{CF}_2$

0.8 g of benzoyl peroxide

Initial Condition T = 25°C P = 140 psi

Maximum T = 110°C P = 250 psi

Final T = 25°C P = 130 psi

Conversion 21%

Yield 8.7 g of sodium salt

IV. 105 g (0.7 mole) of $\text{CF}_3\text{CF} = \text{CF}_2$

1.0 g of benzoyl peroxide

Initial Condition T = 25°C P = 140 psi

Maximum T = 120°C P = 340 psi

Final T = 25°C P = 100 psi

Conversion 22%

Yield 13.6 g of sodium salt

V. 79 G (0.53 mole) of $\text{CF}_3\text{CF} = \text{CF}_2$

2.0 g of benzoyl peroxide

Initial Condition T = 25°C P = 160 psi

Maximum T = 125°C P = 280 psi

Final T = 25°C P = 120 psi

Conversion 28%

Yield 6.8 g of sodium salt

1,1,2,3,3,3-Hexafluoropropanesulfonic Acid

19.4 g of the sodium salt from trials II and III was acidified with an excess of 35% sulfuric acid. The solution was extracted several times with ether. The ethereal extracts were collected, dried over anhydrous sodium sulfate, the ether was removed, and the residue vacuum distilled yielding 10.3 g of a slightly yellow, very viscous product of b.p. 102-103°C/1.2 mm. The compound was redistilled, the fraction boiling at 110-112°C/2.7 mm was collected. The product (9.6 g) was a colorless, viscous, and hygroscopic liquid. Neutralization equivalent 230 (calcd. 232) ^1H nmr spectrum (D_2O) showed two multiplets at 5.91 and 5.18 ppm. Figure 8.

Addition of Sodium Hydrogen Sulfite to Chlorotrifluoroethylene

A solution of 100 g (0.96 mole) of sodium hydrogen sulfite in 200 ml of distilled water buffered to pH = 5.4 with borax, and 1 g of benzoyl peroxide were placed in a 1 liter Parr pressure reactor. The reactor was evacuated, cooled in dry ice-acetone mixture, and 98.5 g (0.84 mole) of liquified chlorotrifluoroethylene was introduced by suction. The contents were heated to room temperature (25°C, 180 psi) and the heating was continued. At 60-70°C an exothermic reaction started. The reaction mixture was heated at 120°C for 20 hours. The total pressure drop at this temperature was 50 psi. The reaction contents were cooled to room temperature, the unreacted chlorotrifluoroethylene liquified (70.9 g, 28% conversion), the reaction mixture filtered and evaporated to dryness. The residue was extracted with hot absolute ethanol. Evaporation of the ethanol gave 39 g of crude sodium chlorotrifluoroethanesulfonate.

Acidification of Crude Sodium ChlorotrifluoroethanesulfonateWith 35% Sulfuric Acid

The crude salt from previous experiment (39 g) was treated with 200 ml of 35% sulfuric acid and the mixture stirred for $\frac{1}{2}$ hour. The inorganic salts were filtered off and the filtrate extracted several times with ether. The ethereal extract was dried over anhydrous magnesium sulfate, the solvent evaporated, and the residue vacuum distilled. Two fractions were collected:

1. Fraction b.p. $35-45^{\circ}\text{C}/2.1\text{ mm}$ (9.5 g, 17.7% calculated on the reacted chlorotrifluoroethylene) was found to be chlorotrifluoroethanesulfonic acid ethyl ester. Saponification equivalent 238 (calcd. 226.5). ^1H nmr spectrum neat showed methyl group protons at 1.30 ppm (3H, triplet, $J = 6.8\text{ Hz}$) and one proton at 6.43 ppm (1H, split doublet $J_{\text{H},\text{F}\text{ gem}} = 47\text{ Hz}$, $J_{\text{H},\text{F}\text{ vic}} = 3\text{ Hz}$).
2. Fraction b.p. $104-106^{\circ}\text{C}/1.5\text{ mm}$ (11.2 g, 22.3%) found to be chlorotrifluoroethanesulfonic acid monohydrate. The compound is a colorless, very viscous, hygroscopic liquid, neutralization equivalent 217 (calcd. 216.5) ^1H nmr spectrum (D_2O) showed a split doublet at 6.67 ppm ($J_{\text{H},\text{F}\text{ gem}} = 47\text{ Hz}$, $J_{\text{H},\text{F}\text{ vic}} = 3\text{ Hz}$). Figure 9.

Hydrolysis of Chlorotrifluoroethanesulfonic Acid Ethyl Ester

Four grams of preceding ethyl ester and 4 ml of water were refluxed for one hour. The water was evaporated, and the residue vacuum distilled yielding 3 g (78%) of chlorotrifluoroethanesulfonic acid, b.p. $104-105^{\circ}\text{C}/1.5\text{ mm}$.

The ir spectrum of the product was identical with that of the sample obtained by acidification of the sodium salt.

Reaction of Chlorotrifluoroethanesulfonic Acid With Ethyl Ether

Three grams of chlorotrifluoroethanesulfonic acid, 20 ml of ethyl ether and 10 g of anhydrous magnesium sulfate were refluxed with stirring for 12 hours. The reaction mixture was filtered, ether evaporated, and the residue vacuum distilled. Two fractions were collected:

1. b.p. 40-45°C/1.1 mm (1.3 g) - identical with the chlorofluoroethane-sulfonic acid ethyl ester described above.
2. b.p. 100-102°C/1.1 mm (1.4 g) - unchanged chlorotrifluoroethane-sulfonic acid.

Preparation of 2,2,2-Trifluoroethyl ThiocyanateA. From 2,2,2-Trifluoroethyl Methanesulfonate

A solution of 145.8 g (1.8 mole) of sodium thiocyanate in 350 ml of dimethylformamide was brought to reflux and distilled through a 7 inch column packed with helices until the head temperature reached 152°C. 79.5 g (0.45 mole) of 2,2,2-trifluoroethyl methanesulfonate was added to the cooled solution. The reaction mixture was very slowly distilled, and the fraction boiling 90-123°C collected over a period of 2.5-3 hours. The distillate was taken up in 300 ml of methylene chloride, washed seven times with 100 ml aliquots of water and twice with brine, and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue vacuum distilled. The fraction boiling 55-70°C/30 mm was collected.

The ¹H nmr spectrum showed about 80% content of the thiocyanate (quartet at 3.45 ppm, J_{H,F} = 10 Hz). The yield of the product corrected for impurities was 31.1 g (48%). Figure 10.

B. From 2,2,2-Trifluoroethyl p-Toluenesulfonate

In a similar experiment, 76.2 g (0.3 mole) of 2,2,2-trifluoroethyl p-toluenesulfonate, 97.2 g (1.2 mole) of sodium thiocyanate and 200 ml of methylene chloride yielded 19.1 g (45%) of the thiocyanate, b.p. 57-72°C/35 mm.

Oxidation of 2,2,2-Trifluoroethyl Thiocyanate With Nitric Acid

Concentrated nitric acid 182 ml (2.77 mole) was placed in a three-necked flask supplied with mechanical stirrer, dropping funnel, thermometer, reflux condenser and a nitrogen inlet tube. 30 g (0.21 mole) of 2,2,2-trifluoroethyl thiocyanate was added very slowly (over 4 hours) at 80-90°C. Nitrogen was continuously bubbled through the reaction mixture to remove the nitrogen oxides formed. The reaction mixture was then heated at 90-95°C (steam bath) until the evolution of nitrogen oxides ceased (about 12 hours). It was then transferred to an evaporating dish and heated on a steam bath. The thick, oily residue was transferred into a distillation flask and vacuum distilled yielding 17.2 g (50%) of 2,2,2-trifluoroethanesulfonic acid. The product is a colorless, hygroscopic solid, b.p. 108-110°C/1.5 mm, m.p. 50-51°C, neutralization equivalent 162 (calcd. 164).

The ¹H nmr spectrum (D_2O) showed a quartet at 3.85 ppm, $J_{H,F} = 10$ Hz.
Figure 11.

Reaction of Partially Fluorinated Alkyl Bromides and Tosylates with Benzyl Mercaptan

In a three-necked flask fitted with mechanical stirrer, thermometer, reflux condenser and dropping funnel were placed 16 g (0.20 mole) of 50% sodium hydroxide and 60 ml of dimethylformamide. The mixture was flushed

well with nitrogen and 24.8 g (0.20 mole) of benzyl mercaptan was added. When homogeneous, the warm solution was treated with 0.17 mole of the partially fluorinated alkyl bromide or tosylate at such a rate as to maintain the reaction temperature at 55-65°C. The solution turned cloudy, and the stirring was continued until the temperature dropped to about 30°C. The reaction mixture was quenched in 250 ml of water, the product extracted with methylene chloride, the organic layer washed with dilute sodium hydroxide and water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue vacuum distilled.

The following compounds were prepared:

1. Benzyl 2-fluoroethyl sulfide was obtained from the corresponding bromide (yield 77%) and tosylate (yield 76%), b.p. 84-85°C/1.5 mm. The ^1H nmr spectrum neat showed aromatic protons at 7.18 ppm (5H, singlet), benzyl protons at 3.60 ppm (2H, singlet) and ethylene protons at 4.67, 3.90, 2.67 and 2.33 ppm (4H, triplets). Figure 12.
2. Benzyl 2,2,2-trifluoroethyl sulfide was prepared from the corresponding tosylate (yield 81%), b.p. 45-46°C/0.20 mm. The ^1H nmr spectrum showed methylene protons at 2.68 ppm (2H, quartet, $J_{\text{H},\text{F}} = 10$ Hz), benzyl protons at 3.61 ppm (2H, singlet), and aromatic protons at 7.14 ppm (5H, singlet).
3. Benzyl 2,2,3,3-tetrafluoropropyl sulfide was prepared from the corresponding bromide (yield 79%) and tosylate (yield 75%) b.p. 69-71°C/0.15 mm. The ^1H nmr spectrum neat showed methylene protons at 2.72 ppm (2H, triplet, $J_{\text{H},\text{F}} = 16$ Hz), benzyl protons at 3.67 ppm (2H, singlet), methine proton at 5.78 ppm (1H, split triplet, $J_{\text{H},\text{F}\text{ gem}} = 53$ Hz, $J_{\text{H},\text{F}\text{ vic}} = 5$ Hz), and aromatic protons at 7.18 ppm (5H, singlet). Figure 14.

Reaction of Partially Fluorinated Alkyl Tosylates with Tert-butyl Mercaptan

In a similar fashion 0.34 mole of 50% sodium hydroxide, 125 ml of dimethylformamide, 30.7 g (0.34 mole) of tert-butyl mercaptan, and 0.17 mole of the corresponding tosylate gave the following sulfides:

1. Tert-butyl 2-fluoroethyl sulfide, yield 65%, b.p. 73-77°C/95 mm. The ^1H nmr spectrum (neat) showed ethylene protons at 4.82, 4.03, 2.92 and 2.63 ppm (4H, triplets), and tert-butyl protons at 1.32 ppm (9H, singlet). Figure 15.
2. Tert-butyl 2,2,2-trifluoroethyl sulfide, yield 55%, b.p. 70-72°C/100 mm. The ^1H spectrum (neat) showed the tert-butyl protons at 1.30 ppm (9H, singlet) and methylene protons at 3.10 ppm (2H, quartet, $J_{\text{H},\text{F}} = 11 \text{ Hz}$). Figure 16.
3. Tert-butyl 2,2,3,3-tetrafluoropropyl sulfide yield 45%, b.p. 63-65°C/100 mm. The ^1H nmr spectrum (neat) showed the tert-butyl protons at 1.30 ppm (9H, singlet), the methylene protons at 3.05 ppm (2H, triplet $J_{\text{H},\text{F}} = 16 \text{ Hz}$), and the methine proton at 5.92 ppm (1H, split triplet $J_{\text{H},\text{F} \text{ vic}} = 53 \text{ Hz}$). Figure 17.

Oxidation of the Sulfides With $\text{Cl}_2/\text{H}_2\text{O}$

In a three-necked flask equipped with mechanical stirrer, thermometer, reflux condenser, and chlorine inlet tube were placed 0.12 mole of the preceding sulfide and 50 ml of water. The mixture was cooled in a dry ice-acetone bath. At 0°C, with ice beginning to form on the walls, gaseous chlorine was added above the mixture, controlling the temperature to -5°C to 0°C generally, with -10°C reached toward the end. Chlorine was introduced until saturation obtained. The lower layer was mixed with 10 ml of

methylene chloride, drained, and chilled while drying over anhydrous magnesium sulfate. Methylene chloride was removed, and the residue distilled under reduced pressure.

The following compounds were prepared:

1. 2-Fluoroethanesulfonyl Chloride

a. From benzyl 2-fluoroethyl sulfide, the product was obtained as a mixture with benzyl chloride, b.p. 80-83°C/25 mm, yield 68% (estimated by nmr spectrum). Figure 18.

b. From tert-butyl 2-fluoroethyl sulfide, yield 56%, b.p. 76-78°C/16 mm. The product was contaminated with unidentified admixtures which could not be removed by fractional distillation.

^1H nmr spectrum (neat) showed four triplets at 5.47, 4.67, 4.38 and 3.98 ppm. Figure 19.

2. 2,2,2-Trifluoroethanesulfonyl Chloride

a. From benzyl 2,2,2-trifluoroethyl sulfide, yield 57%, b.p. 65-67°C/45 mm. The product was contaminated with a small amount of benzyl chloride. Figure 20.

b. From tert-butyl 2,2,2-trifluoroethyl sulfide, yield 61%, b.p. 57-60°C/40 mm (lit. (15) b.p. 64-67°C/45 mm). The product was contaminated by unidentified admixtures which could not be removed by fractional distillation. ^1H nmr spectrum (neat) showed a quartet at 4.37 ppm, $J_{\text{H},\text{F}} = 9$ Hz. Figure 21.

3. 2,2,3,3-Tetrafluoropropanesulfonyl Chloride

a. From benzyl 2,2,3,3-tetrafluoropropyl sulfide the product was obtained as a mixture with benzyl chloride, b.p. 70-75°C/15 mm, yield 63% (estimated by nmr spectrum). Figure 22.

3. b. From tert-butyl 2,2,3,3-tetrafluoropropyl sulfide yield 47%, b.p. 70-77°C/12 mm. The product was contaminated with unidentified admixtures which could not be removed by fractional distillation. ^1H nmr spectrum (neat) showed a split triplet at 5.97 ppm (1H, $J_{\text{H},\text{F}}$ gem = 53 Hz, $J_{\text{H},\text{F}}$ vic = 5 Hz). Figure 23.

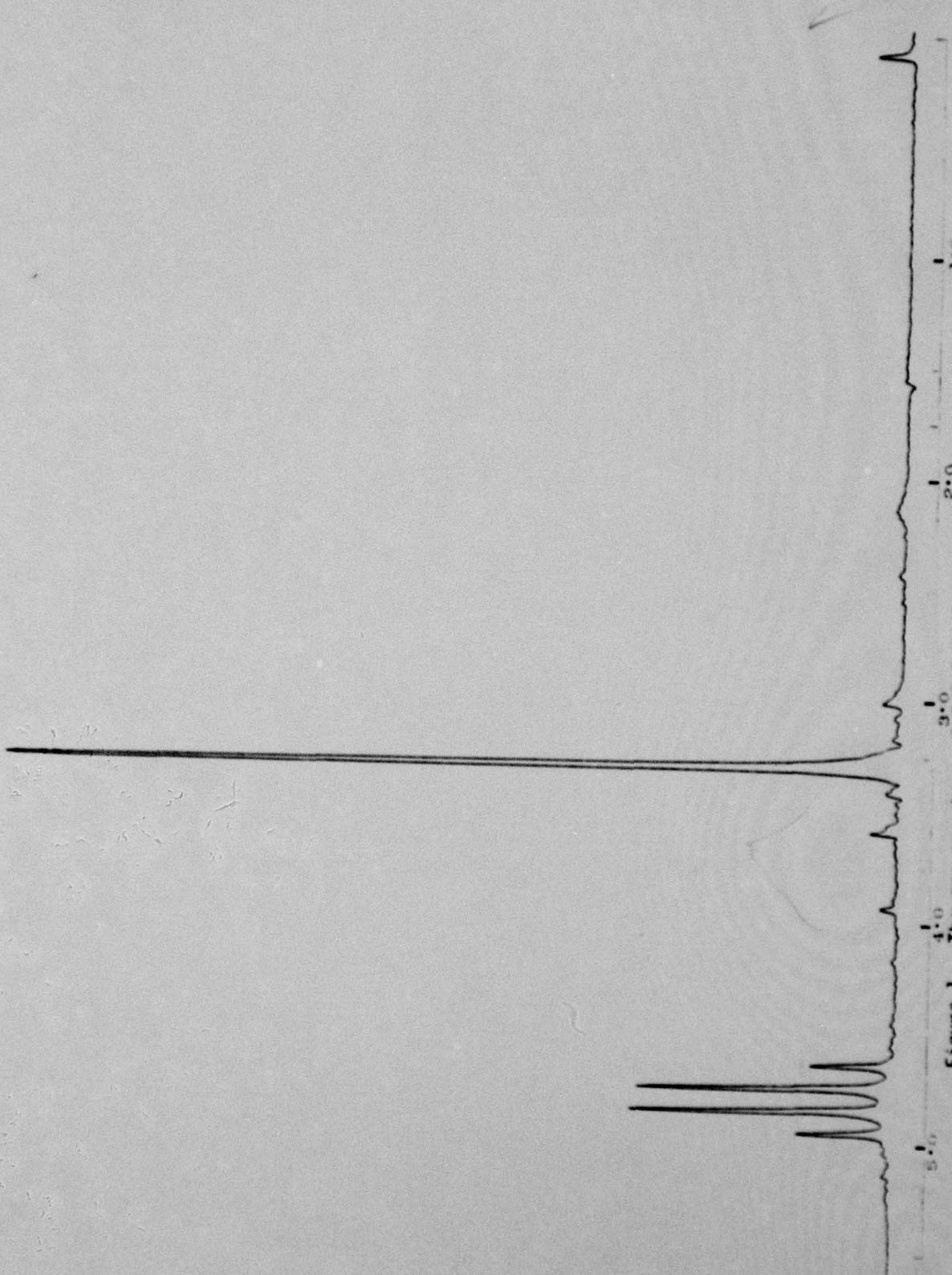
Hydrolysis of Partially Fluorinated Alkanesulfonyl Chlorides to Sulfonic Acids

0.05 mole of the sulfonyl chloride or the appropriate amount of the sulfonyl chloride mixture with benzyl chloride, and 20 ml of water were refluxed with stirring for 10 hours. After cooling the solution was extracted twice with 10 ml aliquots of ether, the aqueous layer was evaporated, and the residue vacuum distilled.

The following sulfonic acids were prepared:

1. 2-Fluoroethanesulfonic acid, yield 66%, b.p. 122-124°C/0.1 mm, neutralization equivalent 127 (calcd. 128). The ^1H nmr spectrum (D_2O) showed ethylene protons as triplets at 5.22, 4.44, 3.54 and 3.12 ppm. Figure 24.
2. 2,2,2-Trifluoroethanesulfonic acid, yield 83%, b.p. 90-93°C/0.1 mm, neutralization equivalent 167 (calcd. 164). The ^1H nmr spectrum (D_2O) showed methylene protons at 3.87 ppm (2H, quartet, $J_{\text{H},\text{F}} = 10$ Hz). Figure 25.
3. 2,2,3,3-Tetrafluoropropanesulfonic acid, yield 83%, b.p. 106-107°C/0.1 mm. neutralization equivalent 200 (calcd. 196). The ^1H nmr spectrum (D_2O) showed the methine proton at 6.01 ppm (1H, split triplet, $J_{\text{H},\text{F}}$ gem = 53 Hz, $J_{\text{H},\text{F}}$ vic = 5 Hz) and methylene protons at 3.53 ppm (2H, triplet, $J_{\text{H},\text{F}} = 16$ Hz). Figure 26.

Figure 1. The nmr spectrum of 2,2,2-Trifluoroethyl methanesulfonate



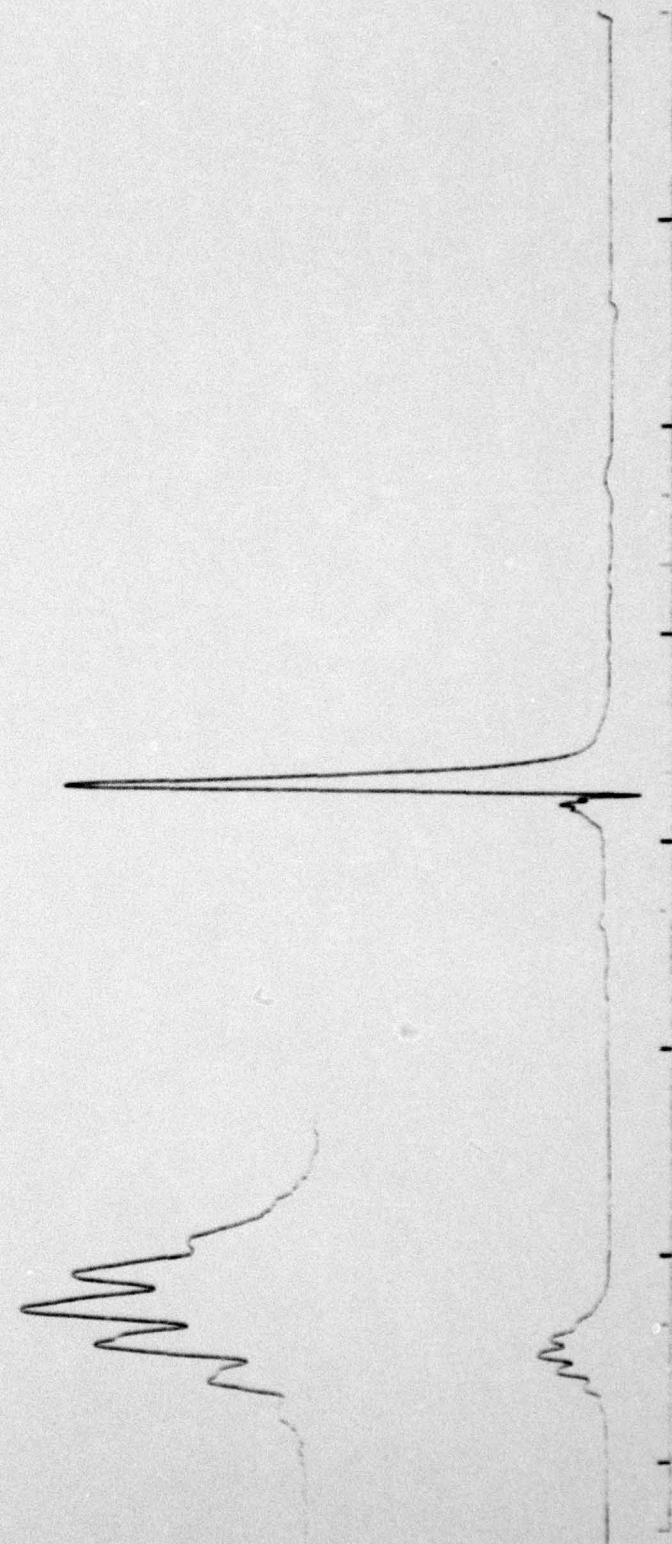


Figure 2. The nmr spectrum of 1,1,1,3,3,3-hexafluoro-2-propyl methanesulfonate

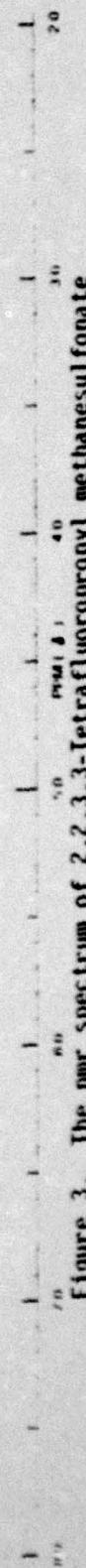


Figure 3. The ^1H NMR spectrum of 2,2,3,3-tetrafluoropropyl methanesulfonate

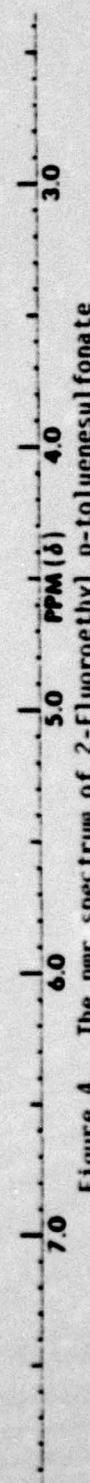


Figure 4. The nmr spectrum of 2-fluoroethyl p-toluenesulfonate

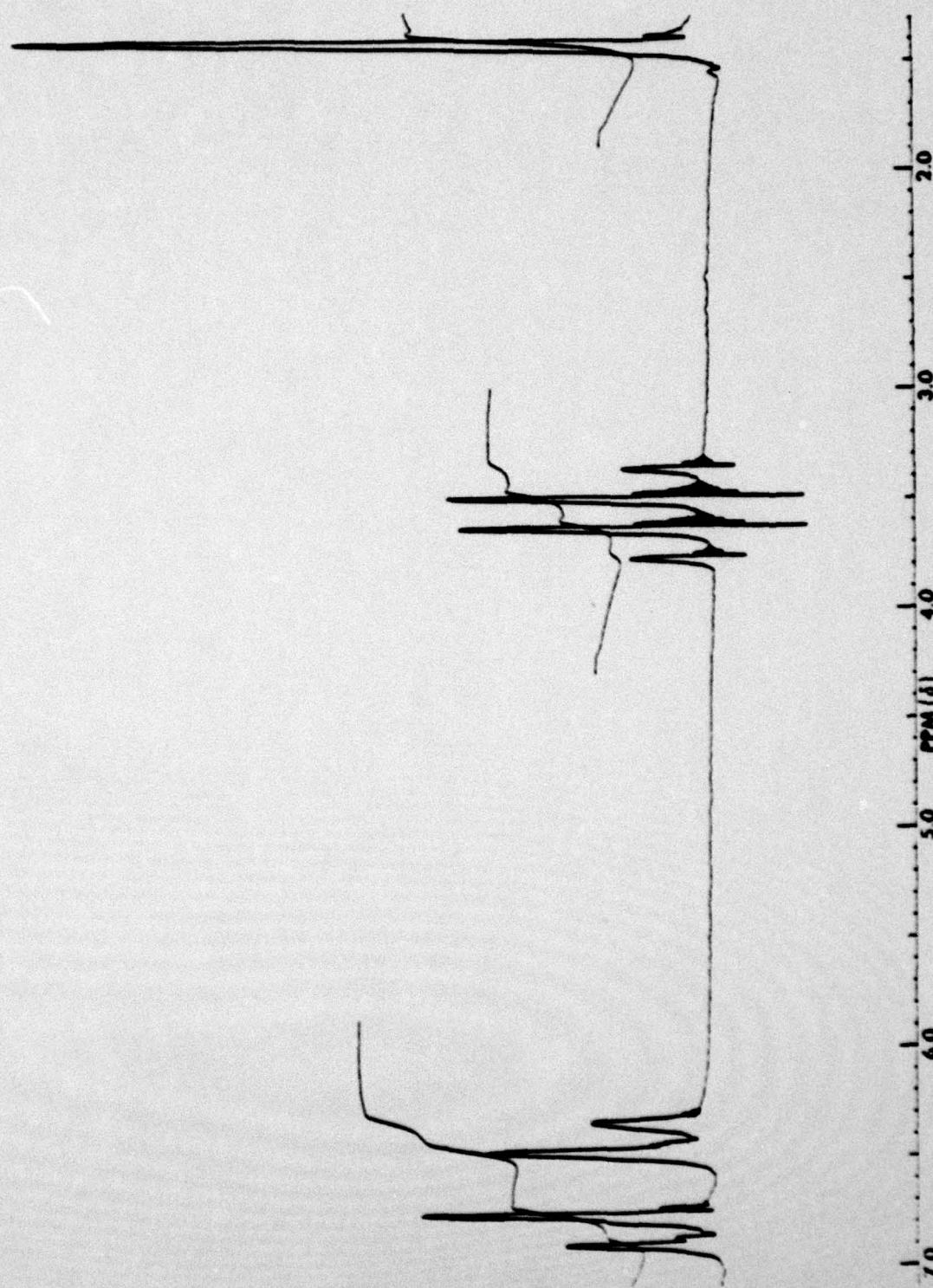


Figure 5. The ^1H NMR spectrum of 2,2,2-Trifluoroethyl p-toluenesulfonate

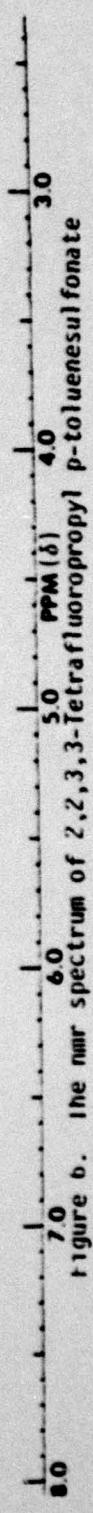


Figure b. The nmr spectrum of 2,2,3,3-tetrafluoropropyl p-toluenesulfonate

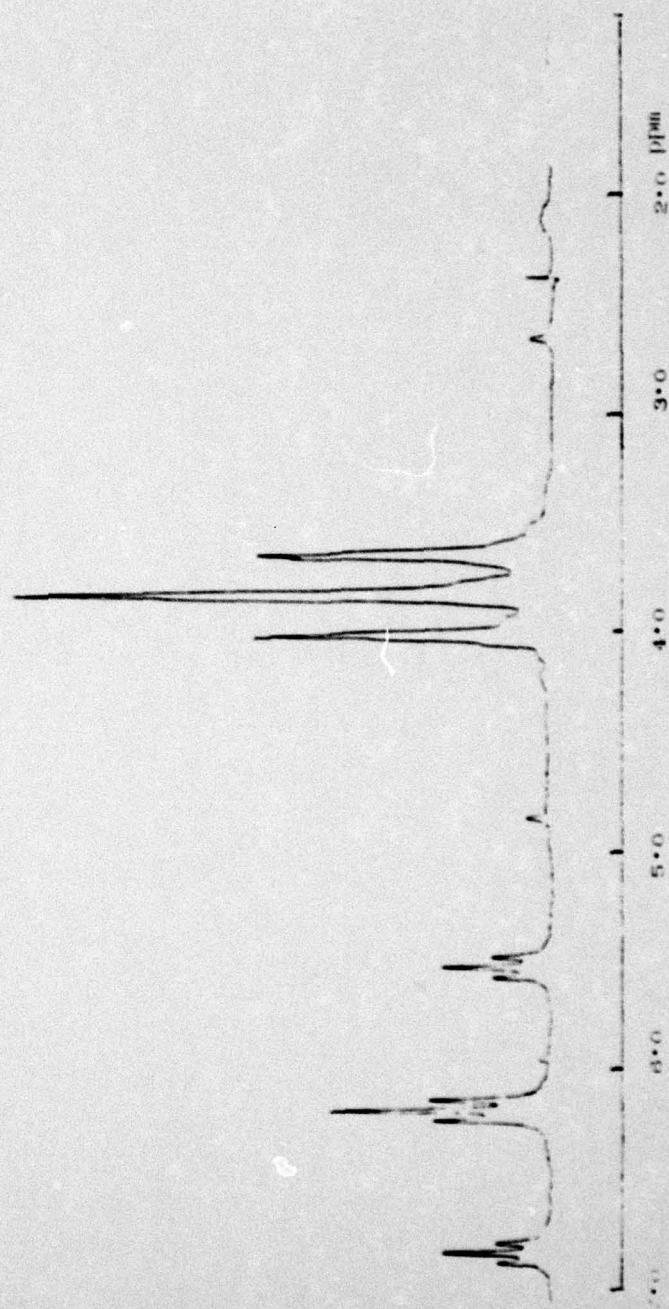


Figure 1. The nmr spectrum of 2,2,3,3-Tetrafluoropropyl bromide

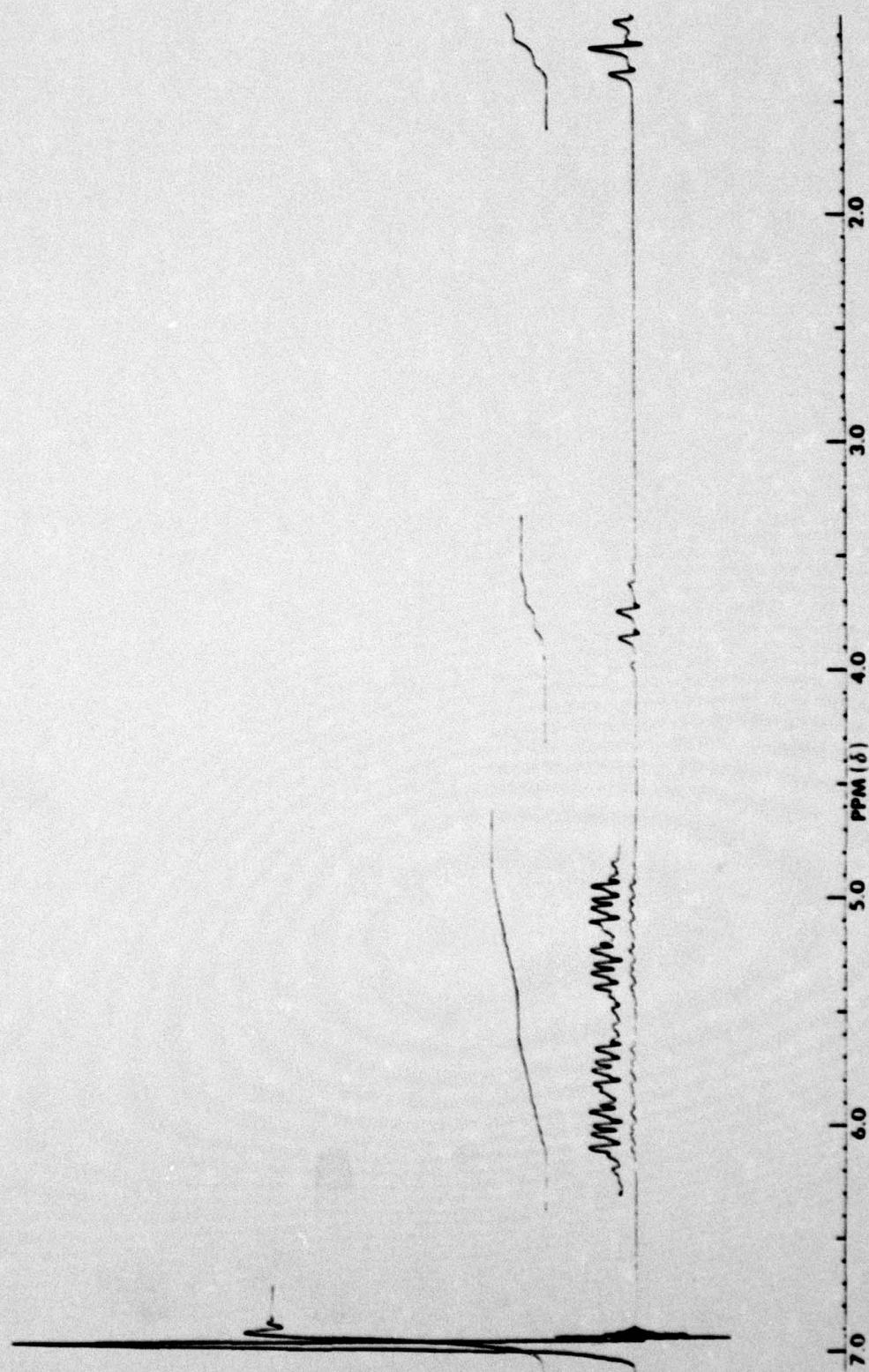


Figure 8. The nmr spectrum of 1,1,2,3,3,3-Hexafluoropropanesulfonic acid

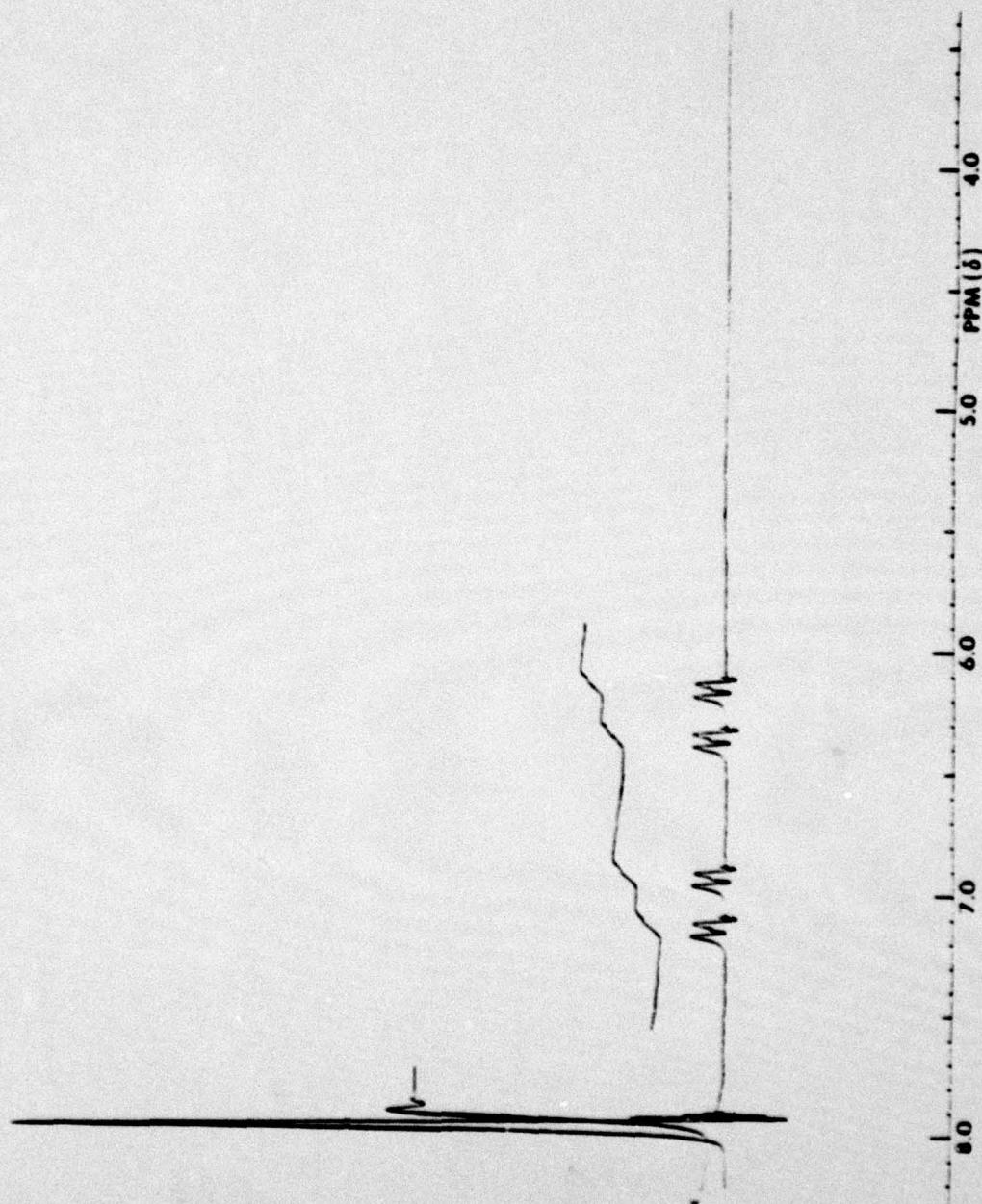


Figure 9. The nmr spectrum of 2-Chloro-1,1,2-trifluoroethanesulfonic acid

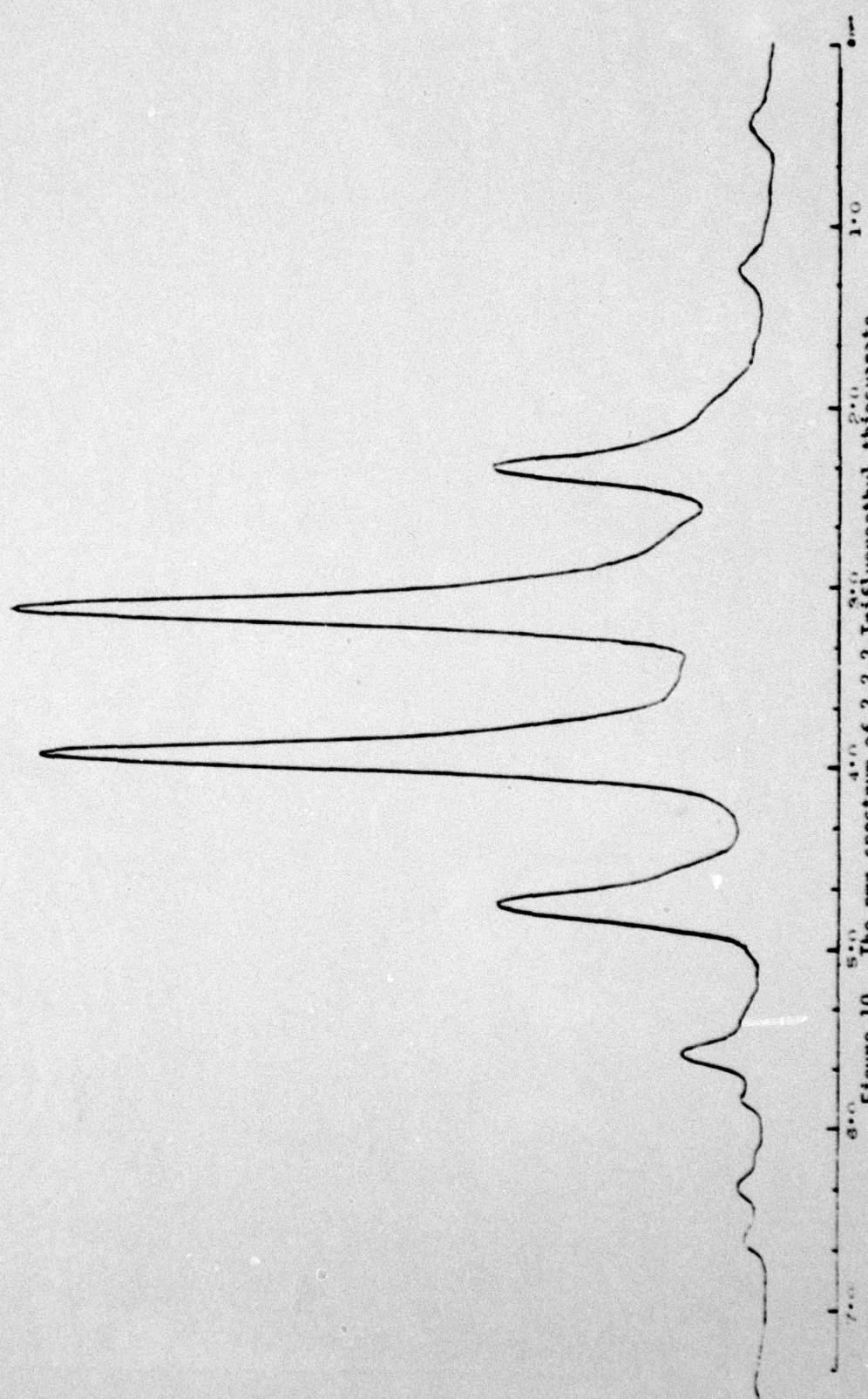


Figure 10. The nmr spectrum of 2,2,2-Trifluoroethyl thiocyanate

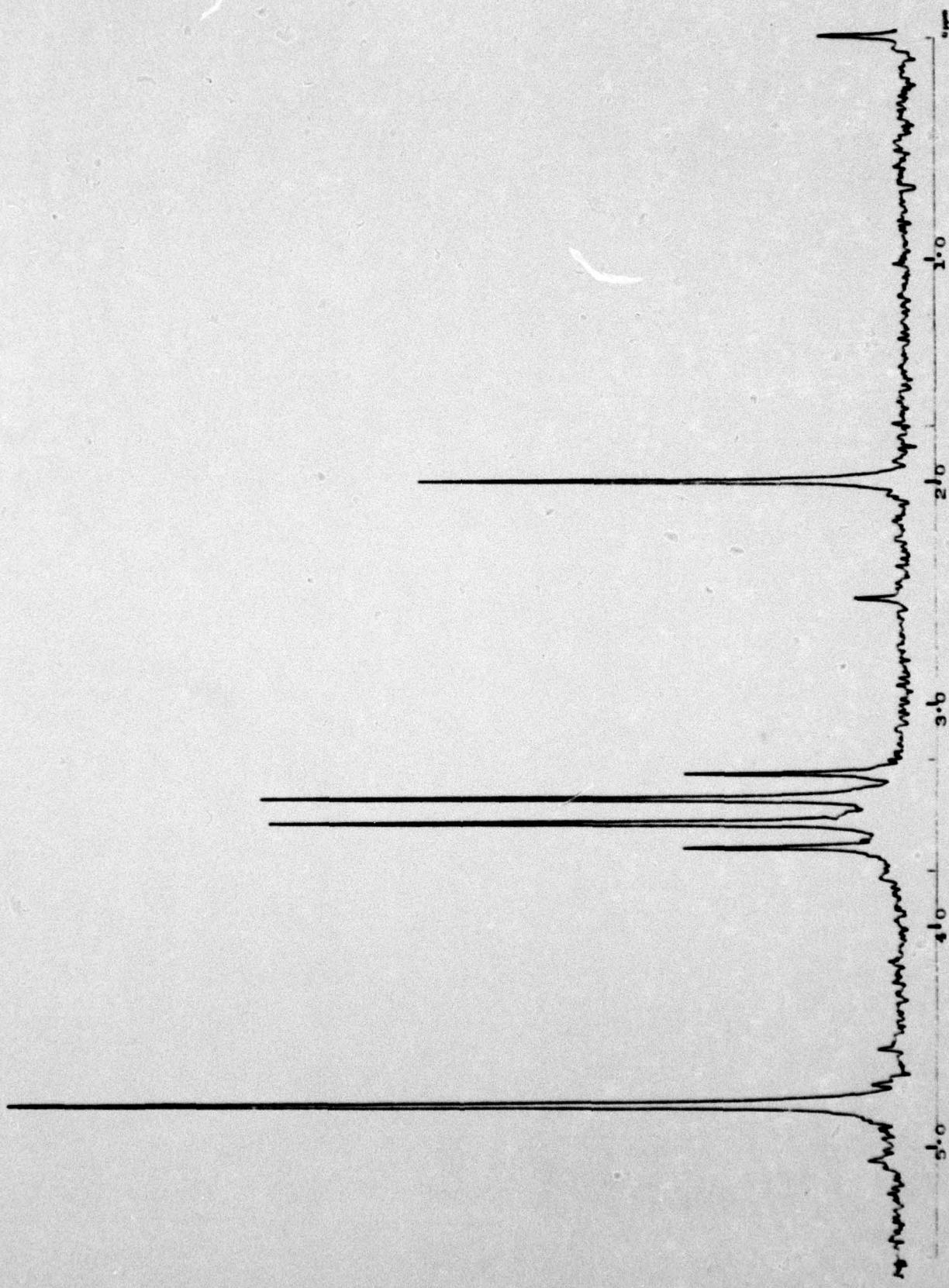


Figure 11. The ¹H NMR spectrum of 2,2,2-Trifluoroethanesulfonic acid

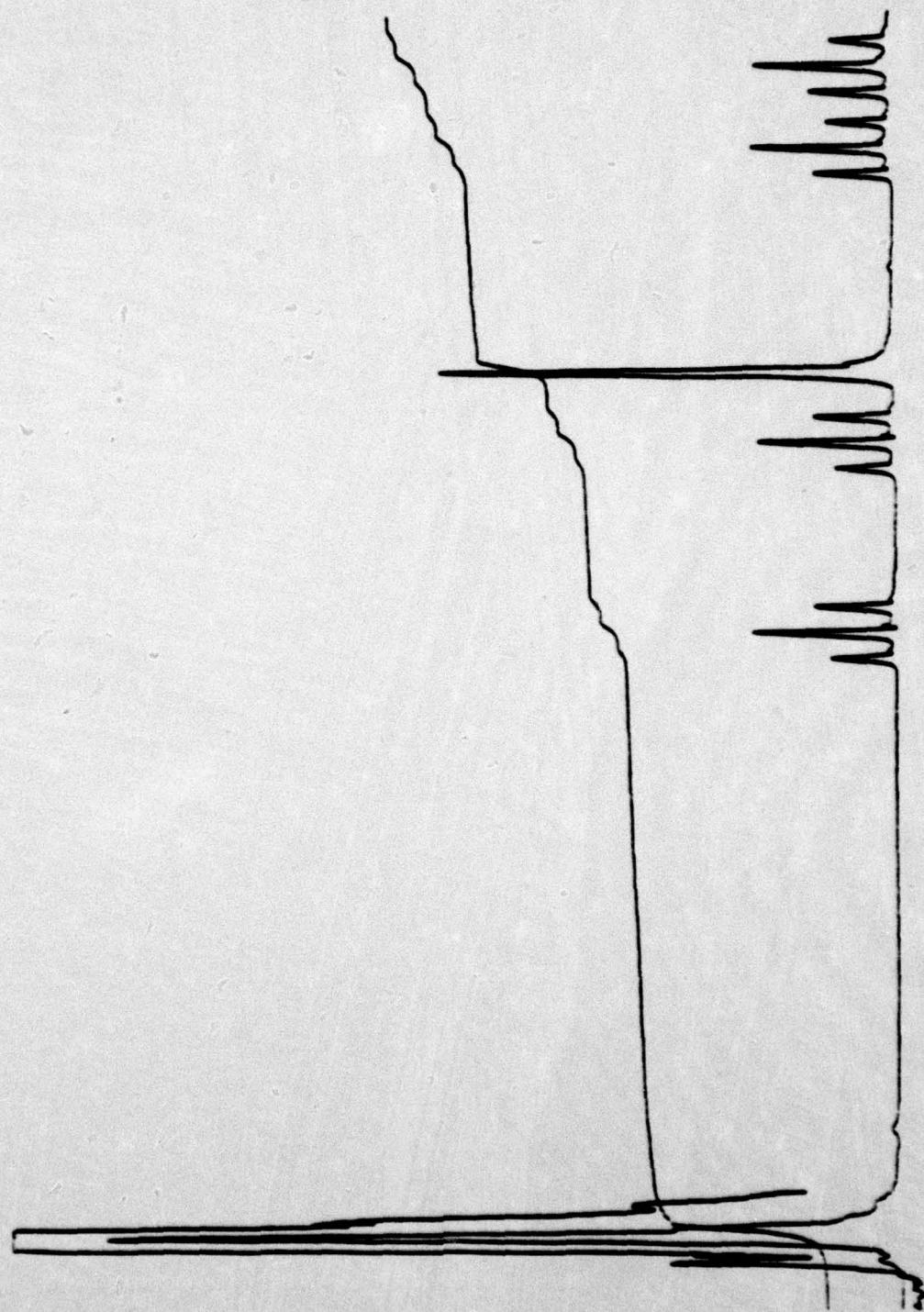


Figure 12." The nmr spectrum of benzyl 2-fluoroethyl sulfide

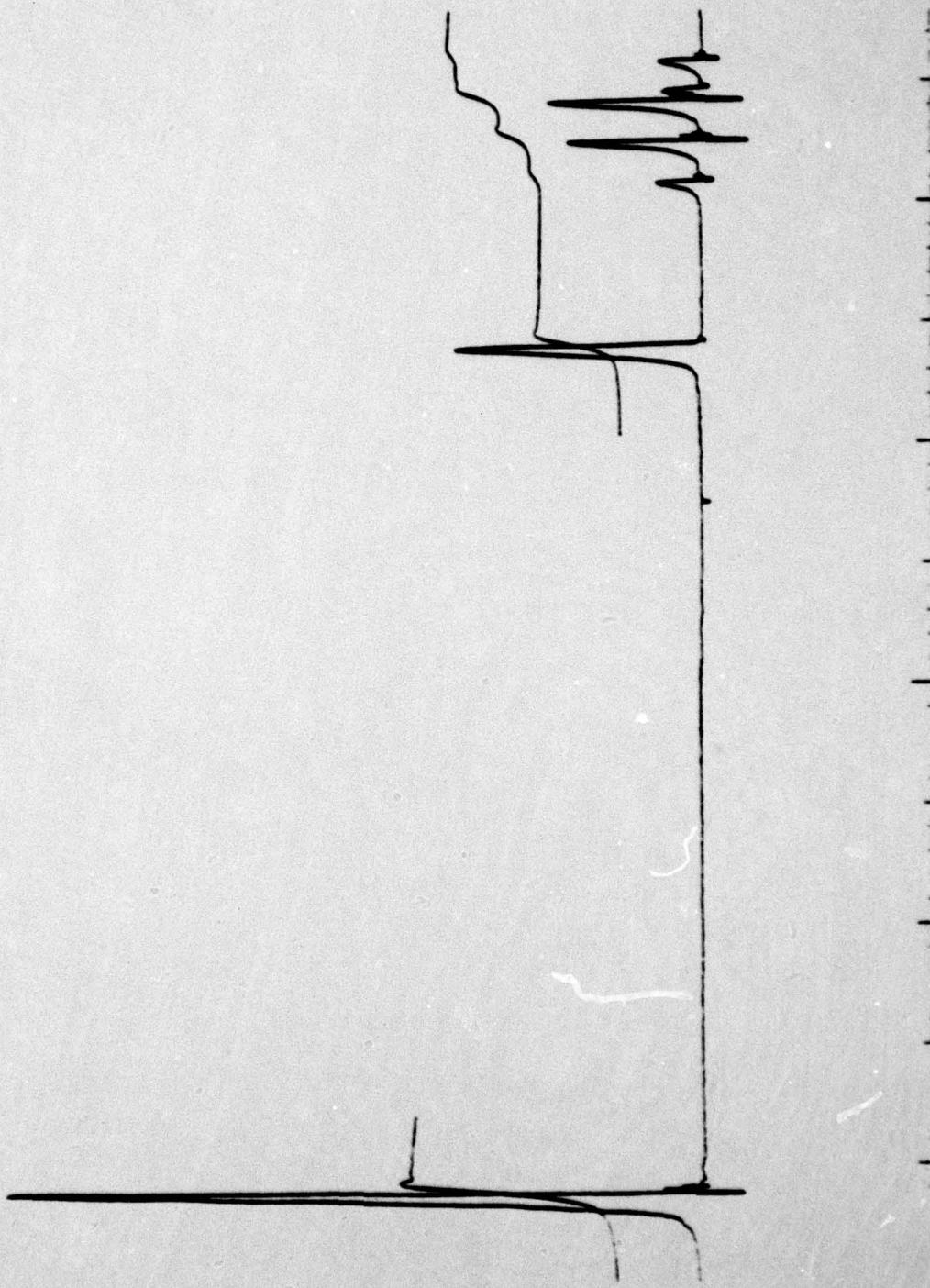


Figure 13. The nmr spectrum of Benzyl 2,2,2-trifluoroethyl sulfide

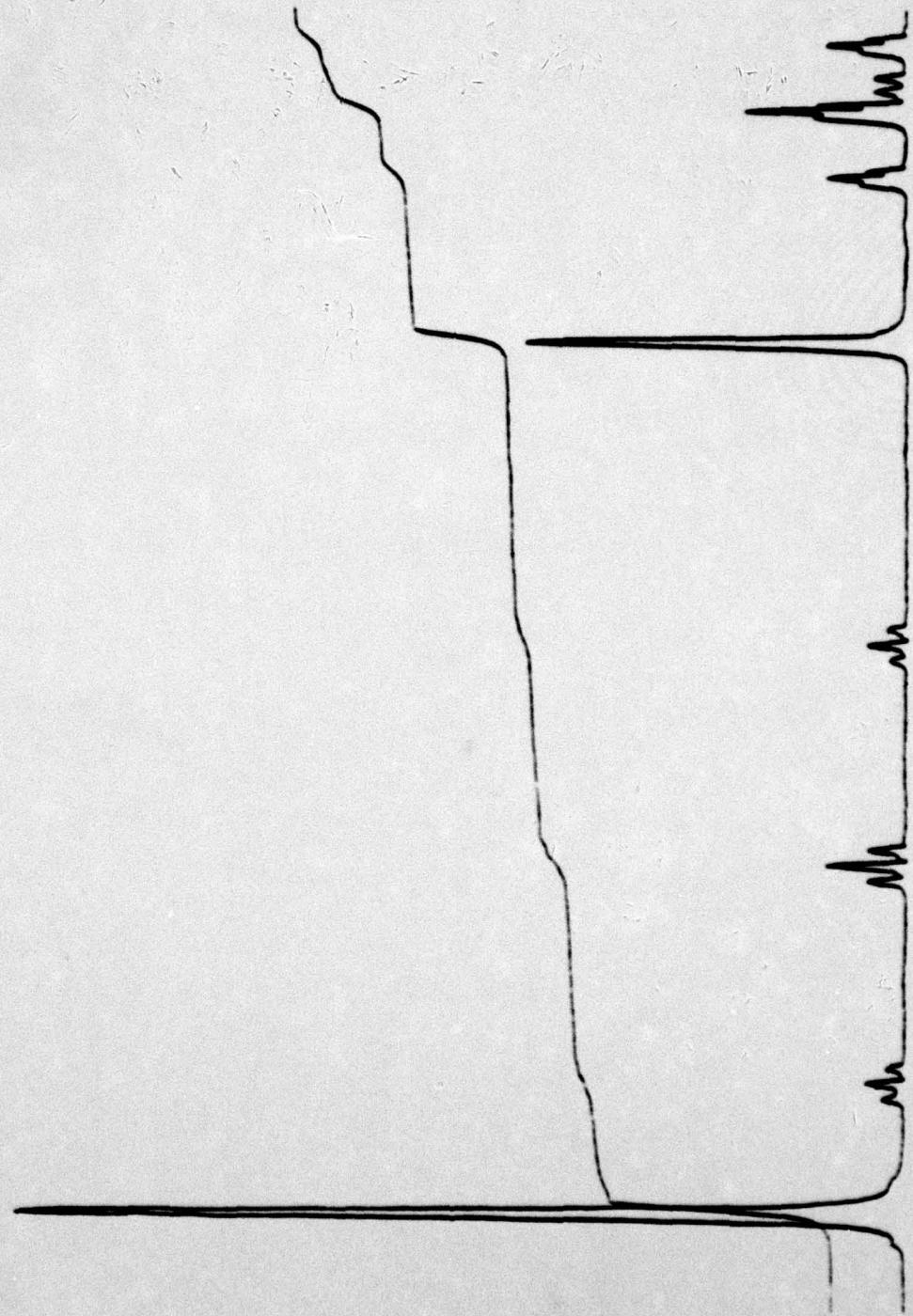


Figure 14. The nmr spectrum of Benzyl 2,2,3,3-tetrafluoropropyl sulfide



Figure 15. The nmr spectrum of Tert-butyl 2-fluoroethyl sulfide

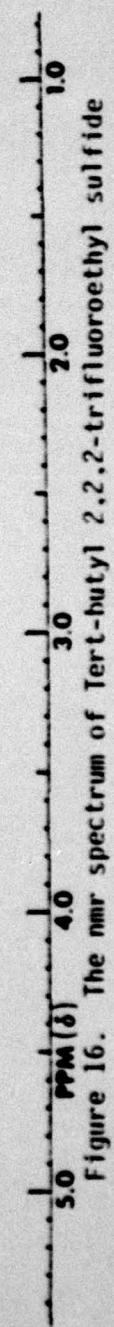


Figure 16. The nmr spectrum of *tert*-butyl 2,2,2-trifluoroethyl sulfide

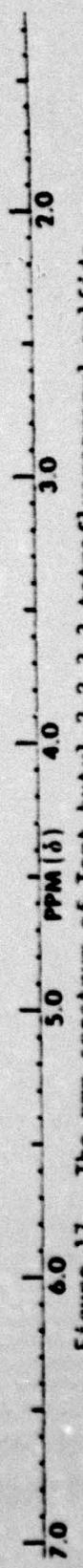


Figure 17. The ^1H NMR spectrum of tert-butyl 2,2,3,3-tetrafluoropropyl sulfide

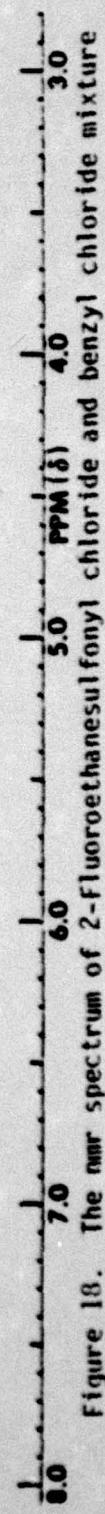


Figure 18. The ^1H NMR spectrum of 2-fluoroethanesulfonyl chloride and benzyl chloride mixture

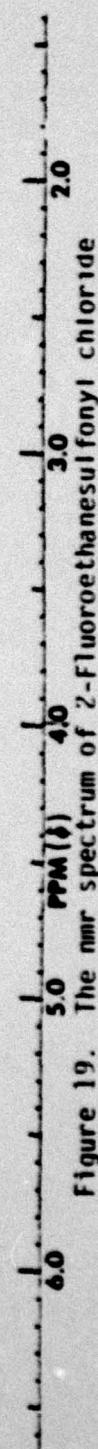


Figure 19. The nmr spectrum of 2-fluoroethanesulfonyl chloride

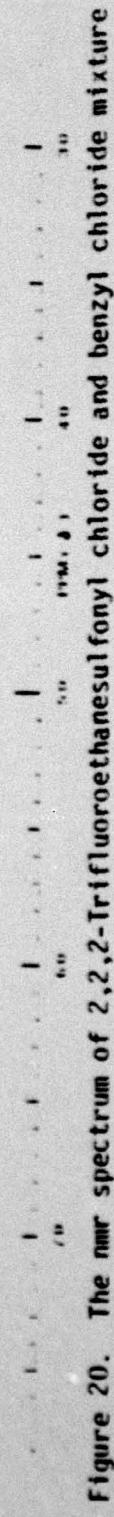


Figure 20. The nmr spectrum of 2,2,2-Trifluoroethanesulfonyl chloride and benzyl chloride mixture

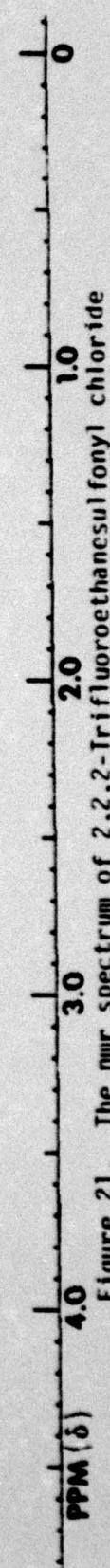


Figure 21. The nmr spectrum of 2,2,2-Trifluoroethanesulfonyl chloride

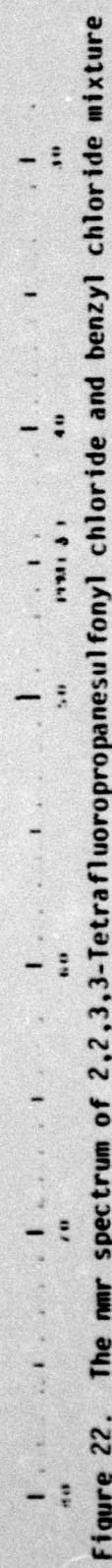


Figure 22. The nmr spectrum of 2,2,3,3-Tetrafluoropropanesulfonyl chloride and benzyl chloride mixture



Figure 23. The nmr spectrum of 2,2,3,3-Tetrafluoropropanesulfonyl chloride



Figure 24. The ^1H NMR spectrum of 2-fluoroethanesulfonic acid



Figure 25. The nmr spectrum of 2,2,2-Trifluoroethanesulfonic acid

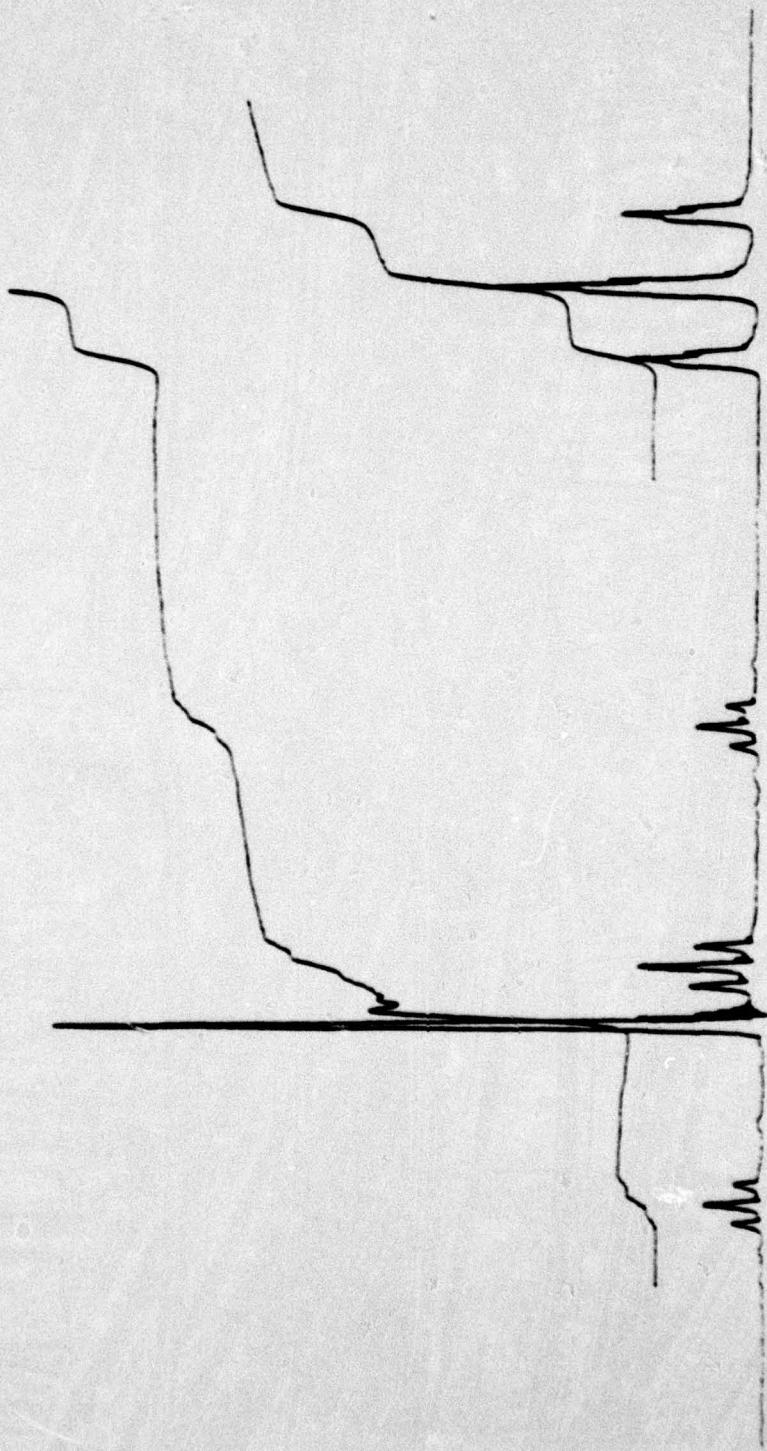


Figure 26. The ^1H NMR spectrum of 2,2,3,3-Tetrafluoropropanesulfonic acid

DISCUSSION

This project was undertaken to find a reasonable method for the synthesis of low molecular weight partially fluorinated alkanesulfonic acids.

According to the literature the following methods looked most promising:

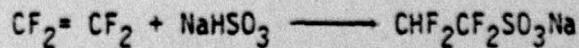
I. Addition of sodium bisulfite to fluorinated alkenes.

II. Exchange of halogen for sulfonic acid group in partially fluorinated alkyl halides.

III. Introduction of sulfur into a partially fluorinated alkyl moiety with subsequent oxidation to a sulfonic acid.

I. Addition of Sodium Sulfite to Fluorinated Alkenes

Almost all of the partially fluorinated alkanesulfonic acids described in the literature were obtained by the addition of sodium bisulfite to fluoroolefins. This method gave good results especially with higher olefins. The general procedure consisted of reacting an aqueous sodium sulfite solution with a fluoroolefin with or without a catalyst (benzoyl peroxide) under autogeneous pressure at 80°-210°C. As far as the low molecular weight partially fluorinated alkanesulfonic acids were concerned, only the preparation of tetrafluoroethanesulfonic acid and hexafluoropropanesulfonic acid were described. For tetrafluoroethanesulfonic acid, Coffmann, Raasch, et al. (3), specified the following reaction conditions: pH 6-7, reaction temperature 120°C and pressure 350 psi.

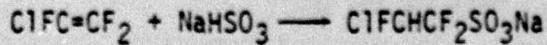


Koshar, Trott and La Zerte (4), obtained hexafluoropropanesulfonic acid in a similar way but they did not specify the volume of the vessel and the reaction pressure. In both cases, the reaction mixture was evaporated to dryness, extracted with alcohol to obtain the alcohol-soluble salts of the sulfonic acids. Tetrafluoroethanesulfonic acid was liberated with 35% sulfuric acid and extracted with ether and then vacuum distilled. Free hexafluoropropanesulfonic acid was obtained by treating the sodium salt with 95% sulfuric acid in sulfan β (SO_3) followed by vacuum distillation of this mixture.



In our preliminary experiments in the preparation of hexafluoropropane-sulfonic acid, using the described amounts of starting materials and carrying out the reaction in a 1 liter Parr reactor, a much lower conversion of hexafluoropropene was achieved. The best results were obtained when an excess of hexafluoropropene and a slightly increased amount of benzoyl peroxide were used. However, the yields and the conversion described by Koshar, Trott and La Zerte were never reached.

The sodium salt of hexafluoropropanesulfonic acid was isolated from the evaporated reaction mixture by extraction with alcohol, but it was found that the best method for conversion of the sodium salt into the free acid was not by treatment with 95% sulfuric acid and sulfan β (SO_3) but rather by treatment with 35% sulfuric acid and subsequent extraction with ether. The best conversion obtained was 22.5%, and the highest overall yield was 11.8%, compared to 84.8% conversion and 63.8% overall yield given by the authors.

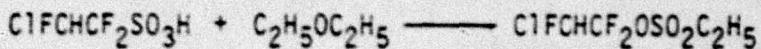


To evaluate the reaction conditions for the addition of sodium hydrogen sulfite to chlorotrifluoroethylene, the olefin was charged in both gaseous and liquified forms. The reaction was carried out at 120°C, 170°C, and 200°C, with and without benzoyl peroxide as a catalyst at pH 5.4, 6-7 and 7-7.5. The details are given in the experimental section. The best results were obtained when chlorotrifluoroethylene was charged in the liquified form, benzoyl peroxide was used as a catalyst, the reaction temperature was 120°C, and the pressure was 240 psi. The conversion of the crude sodium chlorotri-fluoroethanesulfonate was 28% and the yield was 73%.

To convert the sodium salt of chlorotrifluoroethanesulfonic acid into the free acid, two methods were employed: acidification by 35% sulfuric acid followed by extraction with ether and purification by a vacuum distillation; and an ion-exchange method in which a 5-10% aqueous solution of the salt was passed through a column packed with Amberlite IR-120 resin, the aqueous solution of the acid was then evaporated and vacuum distilled. The pure acid could be obtained by both methods but acidification with 35% sulfuric acid was chosen principally to avoid evaporation of large amounts of water necessary with the ion exchange method.

Quite unexpectedly, when the ethereal extract of chlorotrifluoroethane-sulfonic acid was worked up, the vacuum distillation of the product gave two fractions: boiling at 35°- 45°C/2.1 mm.Hg. and at 104°-106°C/1.5 mm.Hg. The high boiling fraction was the chlorotrifluorethanesulfonic acid, whereas the low boiling one did not show a sulfonic acid signal in the ir spectrum and its nmr spectrum showed the presence of an ethyl group, indicating that it was the ethyl ester of chlorotrifluoroethanesulfonic acid. This compound when refluxed with water was converted quantitatively into chlorotrifluo-ethanesulfonic acid. In several experiments the amount of ester fraction

was variable, more of it forming when the ethereal extract of the acid was left overnight with the drying agent, indicating that the ester might have been formed in the reaction of chlorotrifluoroethanesulfonic acid with ethyl ether. In fact, when refluxing chlorotrifluoroethanesulfonic acid in ether in the presence of anhydrous magnesium sulfate for 12 hours, a considerable amount of the ethyl ester was formed.



In further experiments, the addition reactions of 1,1-difluoroethylene, trifluoroethylene and tetrafluoroethylene were tried. None of these olefins could be charged into the reactor in the liquified form because of very low boiling points. They were therefore charged in gaseous form at ambient temperatures and then the pressure reactor was heated to 120°C. The highest pressure (200 psi) observed by this procedure was obtained when using 1,1-difluoroethylene.

In the instance of the addition of tetrafluoroethylene, Barrick (1), stresses that the reaction should be carried out at 325-350 psi. These reaction products were not the expected low molecular weight alkanesulfonic acids.

For the three fluoroolefins above, the free acids could not be obtained from the sodium salt by acidification with 35% sulfuric acid and extraction with ether. Only the ion-exchange method was satisfactory. The compounds were high melting (170°-175°C) solids, not very soluble in water. Attempts to determine the neutralization equivalents were not satisfactory.

The properties of the products indicated that a more complex reaction must have occurred, not the simple addition; the compounds were probably polymers rather than low molecular species, and their structures were not determined.

II. Exchange of Halogen for Sulfonic Group in Partially Fluorinated Alkyl Halides (Strecker's Method)

This method is very popular for the synthesis of non-fluorinated alkane-sulfonic acids.

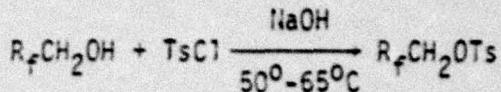
In our preliminary experiments, sodium methanesulfonate, sodium ethanesulfonate, ethane-1,2-disulfonic acid, propane-1,3-disulfonic acid and sodium propane-1,2,3-trisulfonate were prepared in good agreement with the literature data.

Since the halogen atoms in perfluoro and partially fluorinated alkyl halides are much less susceptible to exchange than in their non-fluorinated analogs, Strecker's method was chosen for evaluation in order to establish whether at least some of the partially fluorinated alkanesulfonic acids could be prepared from the corresponding halides.

The reactions of the following halides were investigated: 2,2,2-trifluoroethyl iodide; 2,2,2-trifluoroethyl bromide; 2-fluoroethyl bromide; 2,2,3,3-tetrafluoropropyl bromide; and 2,2,3,3,3-pentafluoropropyl iodide. Since only 2,2,2-trifluoroethyl iodide and 2,2,3,3,3-pentafluoropropyl iodide were commercially available, the other compounds were prepared from the corresponding alcohols via their p-toluenesulfonyl derivatives. One of the alcohols, 2-fluoroethanol had to be prepared from 2-chloroethanol by the method described by Hoffmann (20). This synthesis consisted of reacting 2-chloroethanol with anhydrous potassium fluoride in a mixture of ethylene glycol and diethylene glycol at 170°- 180°C. The yield of 2-fluoroethanol was 50%.

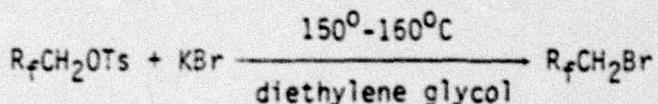
The tosylates were prepared according to the method described by Tiers, Brown and Reid (21), for 2,2,2-trifluoroethyl p-toluenesulfonate. The

alcohol was reacted with p-toluenesulfonyl chloride in water at 50°- 65°C in the presence of sodium hydroxide.

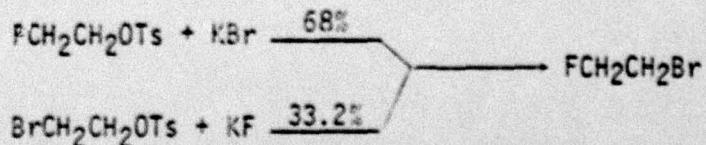


p-Toluenesulfonyl derivatives of 2-fluoroethanol, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol and 2,2,3,3,3-pentafluoropropanol were prepared this way. The yields were very good (80-90%) except for 2-fluoroethanol (35%). For the latter compound better results were obtained (55%) when the reaction was carried out at about 0°C.

The p-toluenesulfonates were converted into their corresponding bromides by the method of Tiers, Brown and Reid (17).



The tosylate was reacted with anhydrous potassium bromide in diethylene glycol at 150°-160°C. The reaction product was distilled from the reaction mixture either under normal or reduced pressure. The yields were also high (70-90%). For 2-fluoroethyl bromide, another method of synthesis was evaluated, the reaction of 2-bromoethyl p-toluenesulfonate and anhydrous potassium fluoride in diethylene glycol at 150°-160°C described by Edgewell and Parts (20).



However, the yield of 2-fluoroethyl bromide prepared from 2-bromoethyl p-toluenesulfonate was much lower.

Three procedures were applied for reacting the above mentioned partially fluorinated alkyl halides.

The first was identical with that used for the synthesis of non-fluorinated alkanesulfonic acids. Sodium sulfite was dissolved in water and the halide was added dropwise at about 50°C with vigorous stirring. The reaction mixture was then refluxed until the halide layer disappeared. Because of the long reaction time, the losses of the halides, especially the lower boiling ones, were unavoidable. This made the results unreliable to some extent and difficult to compare.

In the second procedure, 50% ethanol was used as a reaction medium in such amount as to dissolve the halides completely and the sodium sulfite was only partially dissolved.

The third procedure consisted of carrying out the reaction in a Parr pressure reactor using an aqueous solution of sodium sulfite and introducing the halides by suction into an evacuated reaction vessel. The reaction temperature was 100°C.

The results are tabulated in Table I below:



Yields of Crude Sulfonate Salts

Halide	Reaction		
	In Water	In 50% Ethanol	In Parr Pressure Reactor
CF ₃ CH ₂ I	no reaction	5%	5%
CF ₃ CF ₂ CH ₂ I	no reaction	traces	5%
CF ₃ CH ₂ Br	-	-	10%
CHF ₂ CF ₂ CH ₂ Br	5%	5%	15%
CH ₂ FCH ₂ Br	75%	82%	-

Only 2-fluoroethyl bromide can be used successfully as the starting material for the preparative synthesis of 2-fluoroethanesulfonic acid by this method. The yields of the crude sodium sulfonate were high, but in the preparation of the free acid from the sodium salt only a 23% yield was obtained indicating that the crude salts were highly contaminated.

2,2,2-Trifluoroethyl iodide and 2,2,3,3,3-pentafluoropropyl iodide did not react satisfactorily with sodium sulfite. Very small amounts of sulfonic acid salts, containing sodium iodide probably in the form of double salts, were obtained. This made impossible the conversion of the sodium sulfonates into the free acids because of the presence and further reaction of hydrogen iodide in the acidified mixture. 2,2,2-Trifluoroethyl bromide could be used in Strecker's synthesis only in the Parr pressure reaction because of its very low boiling point (25°C). It seemed to react slightly better than the corresponding iodide.

2,2,3,3-Tetrafluoropropyl bromide gave better results and a sample of pure free 2,2,3,3-tetrafluoropropanesulfonic acid could be prepared from the salt.

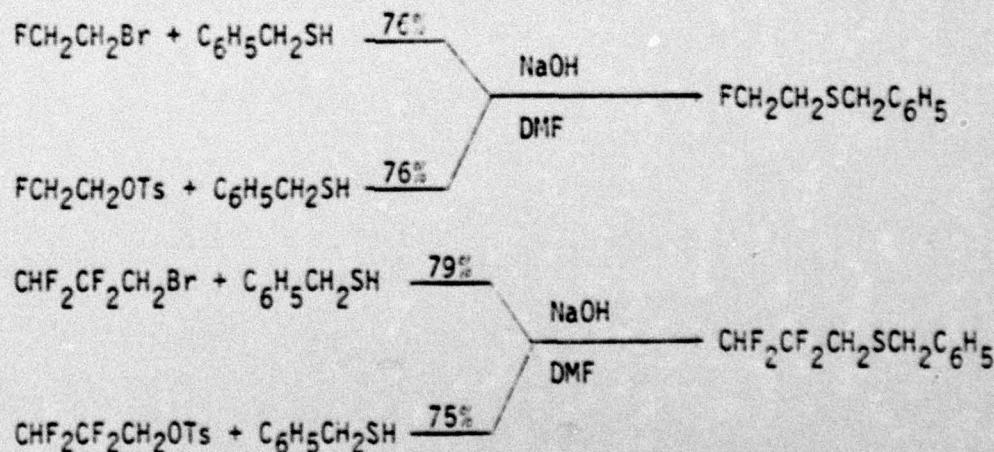
These results indicate that Strecker's method is complicated and inefficient for synthesis of partially fluorinated alkanesulfonic acids. Yields are rather erratic and recovery and purification of the sulfonate salts are very difficult. Even in the instance of 2-fluoroethanesulfonic acid the overall yield (3.4%) is unsatisfactory.

III. Introduction of Sulfur Into A Partially Fluorinated Alkyl Moiety With Subsequent Oxidation to A Sulfonic Acid

Moore (22), described a very convenient method for preparation of fluoromethanesulfonyl chloride and difluoromethanesulfonyl chloride from chlorofluoromethane and chlorodifluoromethane, respectively. These compounds were reacted with the sodium salt of benzyl mercaptan in dimethylformamide to give sulfides. The sulfide when subjected to oxidative chlorination with chlorine in the presence of water produced the sulfonyl chloride. The overall yields in both cases were about 50%.

In our work, an attempt was made to adapt this procedure to the preparation of other partially fluorinated alkanesulfonic acids.

In the first experiment, 2-fluoroethyl bromide and 2,2,3,3-tetrafluoropropyl bromide were reacted with the sodium salt of benzyl mercaptan; the yields of the corresponding sulfides were 76% and 79% respectively. We found that the bromides in this case may be substituted by the tosylates of the corresponding alcohols. The yields were 76% and 75% respectively.

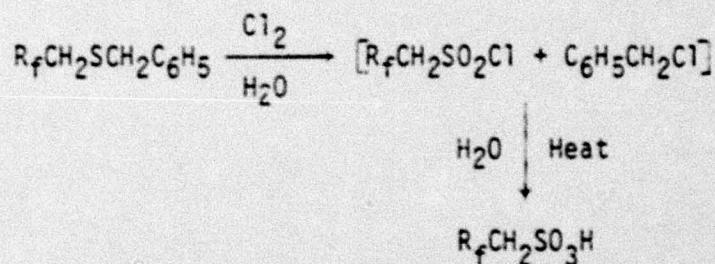
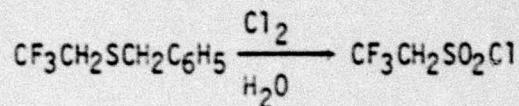


The good results obtained with the tosylates simplified the synthesis because the bromides are usually prepared from the tosylates. The benzyl

2,2,2-trifluoroethyl sulfide and benzyl 2,2,3,3,3-pentafluoropropyl sulfide were prepared only from the tosylates. The yields were 81% and 32%, respectively. In the latter case, further experiments are needed to improve the yield.

All the sulfides are colorless liquids of unpleasant odor. Their structures were confirmed by nmr spectra.

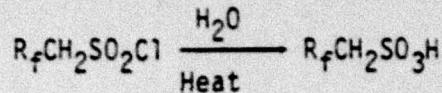
The oxidative chlorination of the sulfides was carried out in water at 0°C by passing chlorine above the surface of the reaction mixture. The reaction is very exothermic and has to be very carefully controlled.



$$\text{R}_f = \text{FCH}_2\text{-}, \text{CHF}_2\text{CF}_2\text{-}, \text{CF}_3\text{CF}_2\text{-}$$

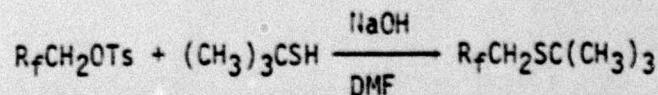
The reaction product, containing sulfonyl chloride and equimolar amounts of benzyl chloride, was extracted with methylene chloride, dried and vacuum distilled. 2,2,2-Trifluoroethanesulfonyl chloride (57%) could be obtained by this method in pure form. 2-Fluoroethanesulfonyl chloride, 2,2,3,3-tetra-fluoropropanesulfonyl chloride and 2,2,3,3,3-pentafluoropropanesulfonyl chloride could not be separated from benzyl chloride by fractional distillation because of the small difference in boiling points. They were used for the next reaction as a mixture with benzyl chloride.

The hydrolysis of the above mentioned sulfonyl chlorides were accomplished by refluxing 2,2,2-trifluoroethanesulfonyl chloride or the mixture of other sulfonyl chlorides with benzyl chloride in water.

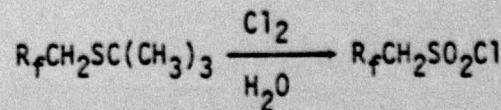


The aqueous solutions of the sulfonic acids were extracted with small amounts of ether to remove the benzyl alcohol and unreacted benzyl chloride, evaporated and vacuum distilled. The yield of 2,2,2-trifluoroethanesulfonic acid was 83%. With 2-fluoroethanesulfonic acid, and 2,2,3,3-tetrafluoropropanesulfonic acid only the overall yield starting from the sulfides could be determined directly. They were 45% and 54% respectively.

Chlorinative cleavage of alkyl sulfides to alkyl chlorides and sulfonyl chlorides occurs readily if the alkyl residue represents a stable cation, e.g. benzyl (23). An attempt was made to substitute benzyl by t-butyl in the sulfides. If the reactions proceeded in similarly good manner the sulfonyl chlorides could be obtained in pure form and there would be no necessity to hydrolyze sulfonyl chloride-benzyl chloride mixtures.



The reaction of 2-fluoroethyl, 2,2,2,-trifluoroethyl, 2,2,3,3-tetrafluoropropyl p-toluenesulfonate with the sodium salt of t-butyl mercaptan proceeded smoothly but gave lower yields (67%, 55% and 52% respectively) even if 100% excess of the mercaptide was used.



Oxidative chlorination of t-butyl partially fluorinated alkyl sulfides gave even poorer results. Not only the yields were lower (FCH_2- , 56%; CF_3- , 61%; CHF_2CF_2- , 47%) but also the products were highly contaminated with unidentified mixtures which could not be separated by fractional distillation. Most probably, t-butyl cation formed in the first of the oxidative chlorination not only combines with chloride anion to form t-butyl chloride but also undergoes other transformations, e.g. elimination, and reacts further with chlorine.

Pure sulfonic acids could be obtained from these sulfonyl chlorides but the yields were again much lower (21-42%).

Comparison of the Method of Preparation of Partially Fluorinated 1-H,1-H-Alkanesulfonic Acids

The results described above are summarized on Schemes I, II and III for each individual sulfonic acid.

2-Fluoroethanesulfonic Acid (Scheme I)

Starting from 2-fluoroethyl p-toluenesulfonate the 2-fluoroethane-sulfonic acid can be prepared by three methods:

- a. Strecker's method via 2-fluoroethyl bromide, sodium 2-fluoroethane-sulfonate (overall yield 12.8%).
- b. In a reaction with benzyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 32.4%).
- c. In a reaction with t-butyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 15.7%).

It should be noted that 2-fluoroethyl p-toluenesulfonate or 2-fluoroethyl bromide are prepared in a rather low yield either from 2-chloroethanol or 2-bromoethanol. For this reason the overall yield given on the scheme are only 3.4%, 9.4% and 4.3%, respectively.

2,2,2-Trifluoroethanesulfonic Acid (Scheme II)

This compound was prepared by two methods. The 2,2,2-trifluoroethanol was converted into the tosylate and then the tosylate was:

- a. reacted with benzyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 34%).
- b. reacted with t-butyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 12%).

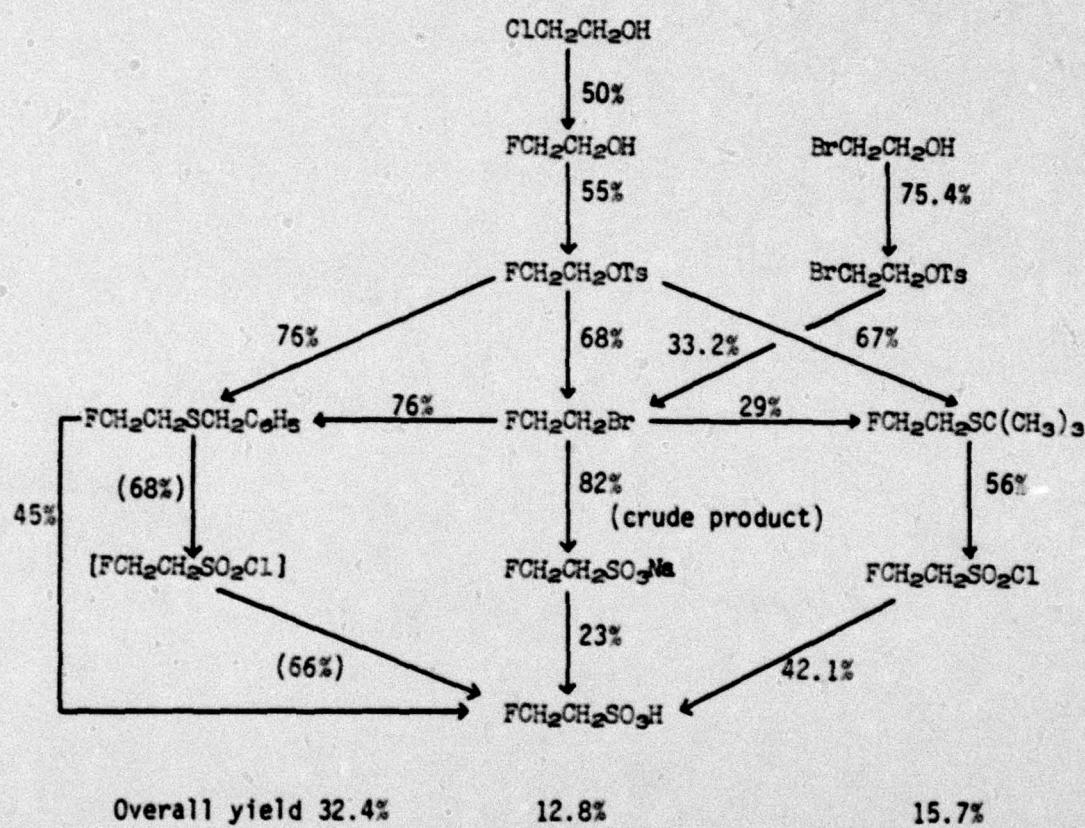
2,2,3,3-Tetrafluoropropanesulfonic Acid (Scheme III)

2,2,3,3-Tetrafluoropropanol was converted into the tosyl derivative which was afterwards:

- a. converted into 2,2,3,3-tetrafluoropropyl bromide followed by reaction with sodium sulfite and acidification (overall yield 6.5%).
- b. reacted with benzyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 33.6%).
- c. reacted with t-butyl mercaptan followed by oxidative chlorination and hydrolysis (overall yield 4.2%).

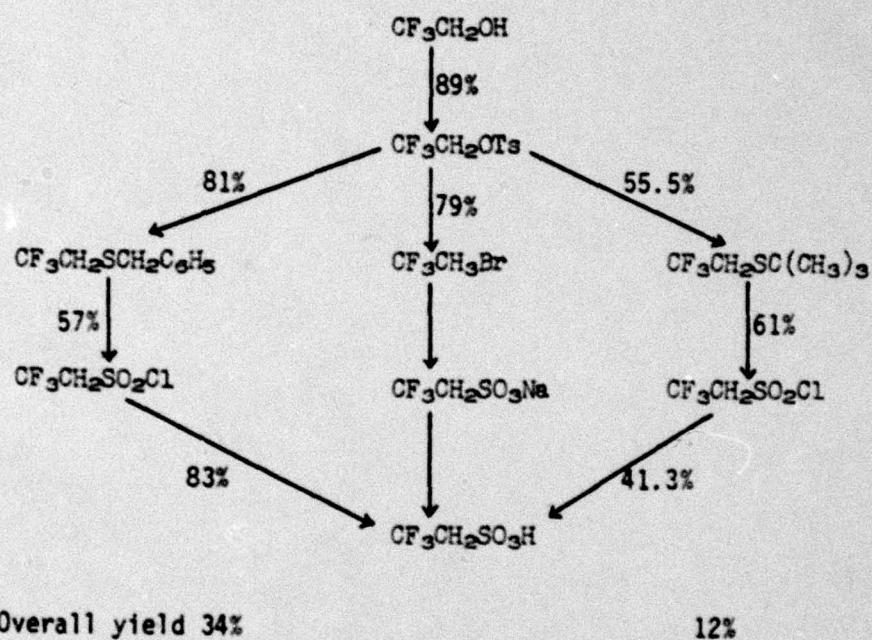
The only conclusion that can be drawn from these data is that the really effective preparative method of synthesis of partially fluorinated 1-H,1-H-alkanesulfonic acids is that proceeding via the benzyl partially fluorinated sulfide.

Scheme I
Preparation of 2-Fluoroethanesulfonic Acid



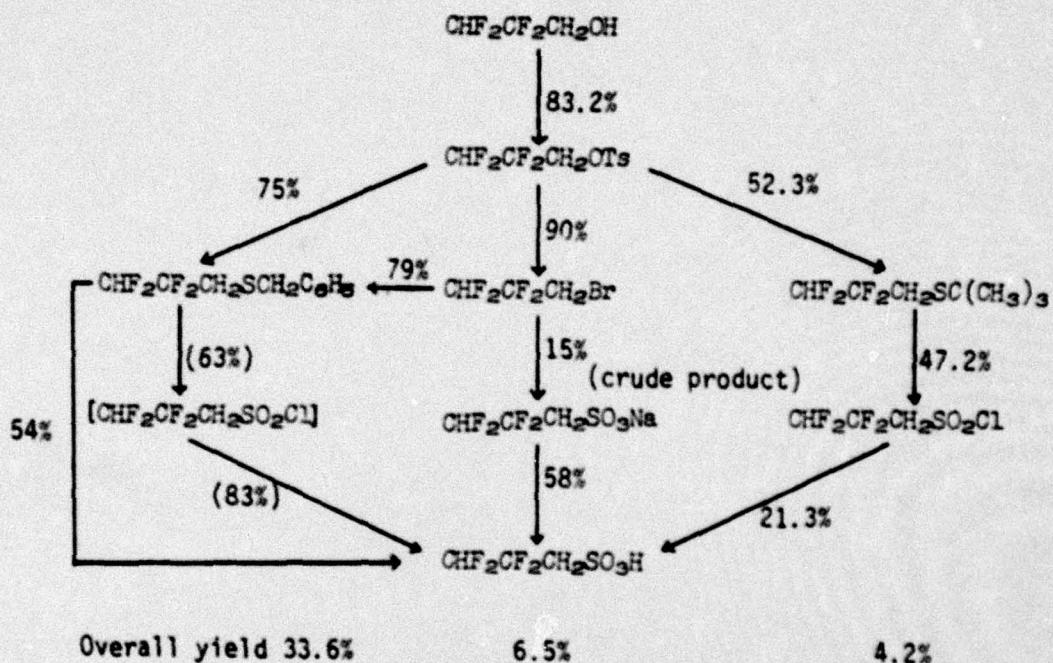
Scheme II

Preparation of 2,2,2-Trifluoroethanesulfonic Acid



Scheme III

Preparation of 2,2,3,3-Tetrafluoropropanesulfonic Acid



CONCLUSIONS

The results obtained enable us to formulate the following conclusions:

1. Low molecular weight partially fluorinated alkanesulfonic acids containing α -methylene groups can be prepared in reasonable yields from the p-toluenesulfonates of the corresponding alcohols, via a reaction with benzyl mercaptan, followed by an oxidative chlorination of the resulting sulfides, with subsequent hydrolysis of the sulfonyl chloride formed.
2. The reaction of partially fluorinated alkyl halides with sodium sulfite (Strecker's Method) proved to be inefficient (very low yields) and unreliable. The sulfonate salts formed are difficult to recover and purify.
3. Addition of sodium bisulfite to fluorinated olefins was found to be effective when the olefin was charged into the reaction vessel in liquified form. The reaction needs further study and investigation for ethylene derivatives.

REFERENCES

1. P.L. Barrick, U.S. Patent 2,403,207 (1946).
2. P.L. Barrick, British Patent 579,897 (1946).
3. D.D. Coffman, M.S. Raasch, et al., J. Org. Chem. 14, 747 (1949).
4. R.J. Koshar, P.W. Trott, and J.D. La Zerte, J. Am. Chem. Soc. 75, 4595 (1953).
5. R.N. Haszeldine, J. Chem. Soc. 1955, 4291.
6. R.N. Haszeldine and J.M. Kidd, J. Chem. Soc. 1954, 4228.
7. Collin, et al., J. Soc. Chem. Ind. (London) 52, 272T (1933).
8. Clarke, Org Synthesis 20.23 (1940); Young, J. Am. Chem. Soc. 59, 811 (1937).
9. Boacker, Rec. Tran. Chem. 54 205 (1935).
10. Murray, J. Chem. Soc. 739 (1933).
11. T.J. Wallace and A. Schriesheim, Tetrahedron, 1965, Vol. 21, pp. 2271 to 2280.
12. R.M. Reed and H.V. Tartar, J. Am. Chem. Soc. 57, 571 (1935).
13. P.H. Latimer and R.W. Bost, J. Org. Chem. 5, 24 (1940).
14. S.M. McElvain, A. Jelinek and K. Rorig, J. Am. Chem. Soc. 67, 1578 (1945).
15. R.K. Crossland, K.L. Servis, J. Org. Chem. 35, 3195 (1970).
16. R.K. Crossland, W.E. Wells, and V.J. Shiner, Jr., J. Am. Chem. Soc. 93, 4217 (1971).
17. W.F. Edgell and L. Parts, J. Am. Chem. Soc. 77, 4899 (1955).
18. A.L. Hene and M.W. Renoll, J. Am. Chem. Soc. 58, 889 (1936).
19. A.L. Hene and R.P. Ruh, J. Am. Chem. Soc. 70, 1025 (1948).
20. H. McCombie and B.C. Saunders, Nature 158, 382 (1946).
21. G.V.D. Tiers, H.A. Brown and T.S. Reid, J. Chem. Soc. 75, 5978 (1953).
22. G.G.I. Moore, J. Org. Chem. 44, 1708 (1979).
23. E.E. Gilbert, "Sulfonation and Related Reactions," Interscience, New York, 1965, p. 201.

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